

Thermal Treatment Technologies: Lessons Learned



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THERMAL TREATMENT TECHNOLOGIES: LESSONS LEARNED

Start	End	Topic
10:30 AM	10:35 AM	Welcome & Introduction (<i>Dr. Hans Stroo</i>)
10:35 AM	11:00 AM	Overview and State of the Practice Summary (<i>Dr. Paul Johnson</i>)
11:00 AM	11:25 AM	Measuring and Modeling Thermal Treatment at Naval Air Warfare Center (<i>Dr. Bernie Kueper</i>)
11:25 AM	11:35 AM	Questions and Open Discussion
11:35 AM	12:05 PM	Simulating Thermal Treatment of Fractured Rock (<i>Dr. Ronald Falta</i>)
12:05 PM	12:20 PM	Effects of Thermal Treatment on the Microbial Reductive Dechlorination Process (<i>Dr. Frank Löffler</i>)
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Critical Evaluation of State-of-the-Art In Situ Thermal Treatment Technologies for DNAPL Source Zone Treatment

ER-200314

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The Business of Innovation



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 - ◆ Eric Foote - Battelle
- Others
 - ◆ Jennifer Triplett Kingston – Arizona State University / Haley & Aldrich
 - ◆ Paul R. Dahlen – Arizona State University
 - ◆ Shane Williams - Battelle



Technical Objective

Develop a tool that can be used by practitioners, regulators, and site owners to anticipate the likely design and performance of thermal-based DNAPL treatment technologies at their sites, including:

- how the technology has been applied in that type of setting,
- the designs employed,
- the operating conditions,
- the performance monitoring that results are based on,
- the performance observed,
- indicators of success at other sites, and
- reasonable bounds on expected performance.



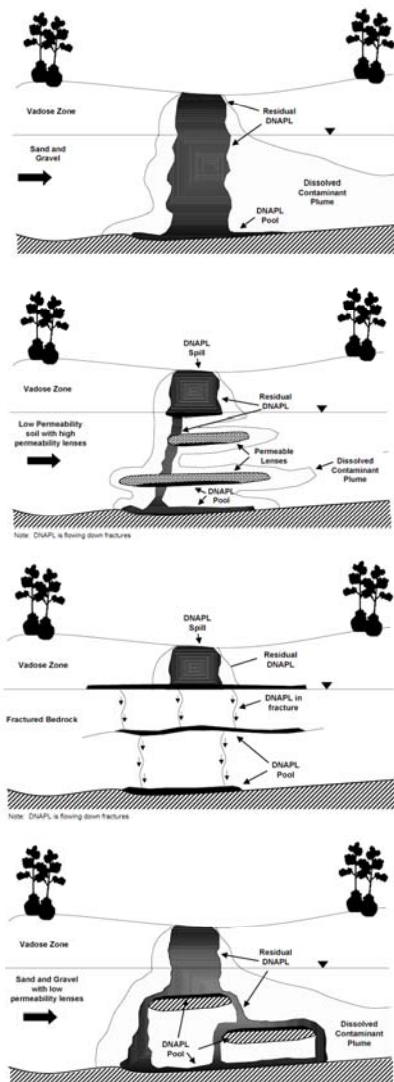
In this project, the performance metrics focus on improvement to **groundwater quality** and reduction in **mass discharge** (flux).

Final Product/Tech-Transfer Concept

Physical Scenarios

Technology Application Summary

Experience/ Performance Summary



Scenario	Technology	# of Sites	# of Pilot Tests	# of Full-Scale Systems	# of Systems Since 2000
Generalized Scenario A: relatively homogeneous and permeable unconsolidated	Steam Heating	7	5	2	2
	Resistance Heating	4	3	0	1
	Other	9	7	1	1
Generalized Scenario C: largely permeable sediments with interbedded lenses of low	Steam Heating	4	0	3	1
	Resistance Heating	12	3	7	3
	Other	7	2	5	3
Generalized Scenario D: largely impermeable sediments with interbedded layers of higher	Steam Heating	17	6	8	7
	Resistance Heating	15	4	8	7
	Other	15	5	9	2
Generalized Scenario E: competent, but fractured bedrock	Steam Heating	3	1	1	1
	Resistance Heating	0	0	1	0
	Other	0	0	0	0
Generalized Scenario F: karst and/or weathered bedrock	Steam Heating	2	2	0	2
	Resistance Heating	0	0	0	0
	Other	0	0	0	0
Generalized Scenario G: unknown	Steam Heating	15	2	5	2
	Resistance Heating	6	0	0	0
	Other	7	3	2	0

This table and others summarize key design and performance attributes, including numbers of energy delivery points, treatment times, temperatures reached, etc.



Technical Approach

Step 1: Collect, review, and compile historical performance data; then, using professional judgment, decide how best to capture the information in user-friendly performance summary tables linked to idealized conceptual models.

Step 2: Conduct supplemental post-treatment field investigations at four to six sites identified in Task 1. Sites to be chosen to best augment the information compiled in Task 1.

Step 3: Synthesize results – Utilize results from this study, other SERDP/ESTCP projects, etc. to identify performance bounds on improvements to groundwater quality and contaminant mass discharge (a.k.a. “mass flux”).

Summary of Applications Identified



Technology	Number of Applications	Pilot-Scale*	Full-Scale*	Number Since Year 2000
Steam-Based	46	26	19	15
Electrical Resistance Heating	87	23	56	48
Conduction	26	12	14	17
Other/Radio-Frequency	23	14	9	4
Total	182	75	98	84

*Some sites have unknown application sizes and thus are not included in the Pilot- and Full-scale counts



Characterization of Documentation

Level of Data Quantity	Description	Number of Sites
-	Application in progress	1
0	No documentation available at the time of this study	26
1	Insufficient data to assess performance of technology, but some design information	78
2	Limited performance data; some soils and/or groundwater concentration data and some operating data (e.g., temperature information)	37
3	Good performance data record, but insufficient for estimating differences between pre- and post mass discharge from source zone	26
4	Data sufficient for full assessment of performance (groundwater concentrations and mass discharge)	14
Total		182

Design and Operating Information

Performance Information

Basic Design Information

Technology	Number of Sites With Target Treatment Zones With Sizes In This Range [ft ²]				Number of Sites With Density of Energy Delivery Points (electrodes or wells) In this Range [# per 100 ft ²]			
	<10 ⁴	10 ⁴ - 4x10 ⁴	<4x10 ⁴	Unknown	<0.25	0.25-0.50	>0.5	Unknown
Steam-Based Heating	16	6	4	20	20	2	4	20
Resistance Heating	36	24	0	27	10	23	27	27
Conductive Heating	19	6	0	1	1	1	23	1
Other (including Mixing/Heating)	8	2	0	13	2	0	8	13

* For the three steam auger sites, the density is one energy point per cell. This does not fit into the number calculation so it is classified as <0.5.

<1/4 acre

<15 ft spacing 11

Basic Operating Conditions

Technology	Number of Sites With Temperatures in Target Treatment Zone in These Ranges [C]				Number of Sites With Active Heating Durations in These Ranges [y]				Number of Sites With Post-Treatment Monitoring in These Ranges [y]			
	<80	80 - 110	>110	Unknown	<0.5	0.5 - 1.0	>1.0	Unknown	<0.5	0.5 - 2.0	>2.0	Unknown
Steam-Based Heating	7	13	1	25	14	0	3	29	2	0	0	44
Resistance Heating	9	37	0	41	38	2	0	47	1	5	1	80
Conductive Heating	0	11*	12*	4	18	3	0	5	1	1	0	24
Other (including Mixing/Heating)	2	2	1	18	6	0	0	17	3	0	0	20

* One site had two different temperature values. The 80-110 C temperature was for the saturated zone and the >110 C temperature for the vadose zone.

Reflection of ↑
technology capabilities

↑ Durations often
decided *a priori*

↑ ?



Geologic Scenarios

- *Scenario A:* relatively homogeneous and permeable unconsolidated sediments (mixtures of sands, gravels and silts, etc.)
- *Scenario B:* largely impermeable sediments with inter-bedded layers of higher permeability material
- *Scenario C:* largely permeable sediments with inter-bedded lenses of low permeability material
- *Scenario D:* competent, but fractured bedrock (i.e. crystalline rock)
- *Scenario E:* weathered bedrock, limestone, sandstone



Thermal Geologic Settings

- The majority of recent thermal applications were conducted in settings matching Generalized Scenario B and C.
- Scenario B accounts for 43% (36 of 84) of thermal treatments, two-thirds of which are ERH applications.
- Scenario C accounts for roughly another one-third (29%) of all applications.



Supplemental Field Investigations

Selection Criteria:

1. The hydrogeology of the site was reasonably well-characterized;
2. The aerial extent of the source zone was reasonably defined prior to treatment;
3. The depth to groundwater was <20 ft;
4. The total depth to impacted groundwater was <40 ft;
5. There was access immediately down-gradient of the treatment zone for drilling;
6. Direct-push technology could be used; and,
7. Local site personnel were present to facilitate the logistics associated with the sampling events.

Fort Lewis

East Gate Disposal
Yard, Area 3,
Ft. Lewis, WA

Naval Air Station,
Building 5,
Alameda, CA

NAS Alameda

Air Force Plant 4,
Ft. Worth, TX

Air Force Plant 4

Camp Lejeune

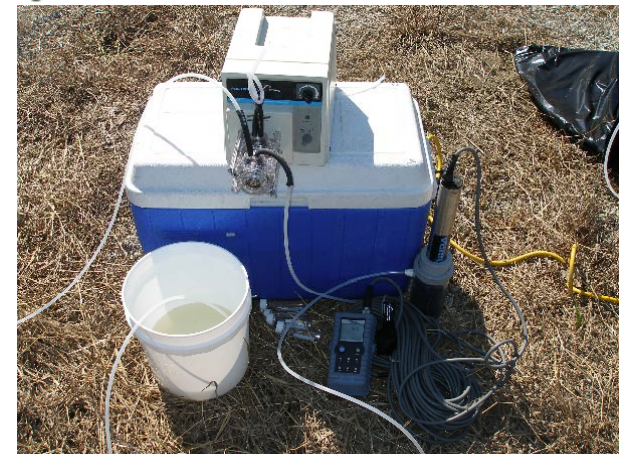
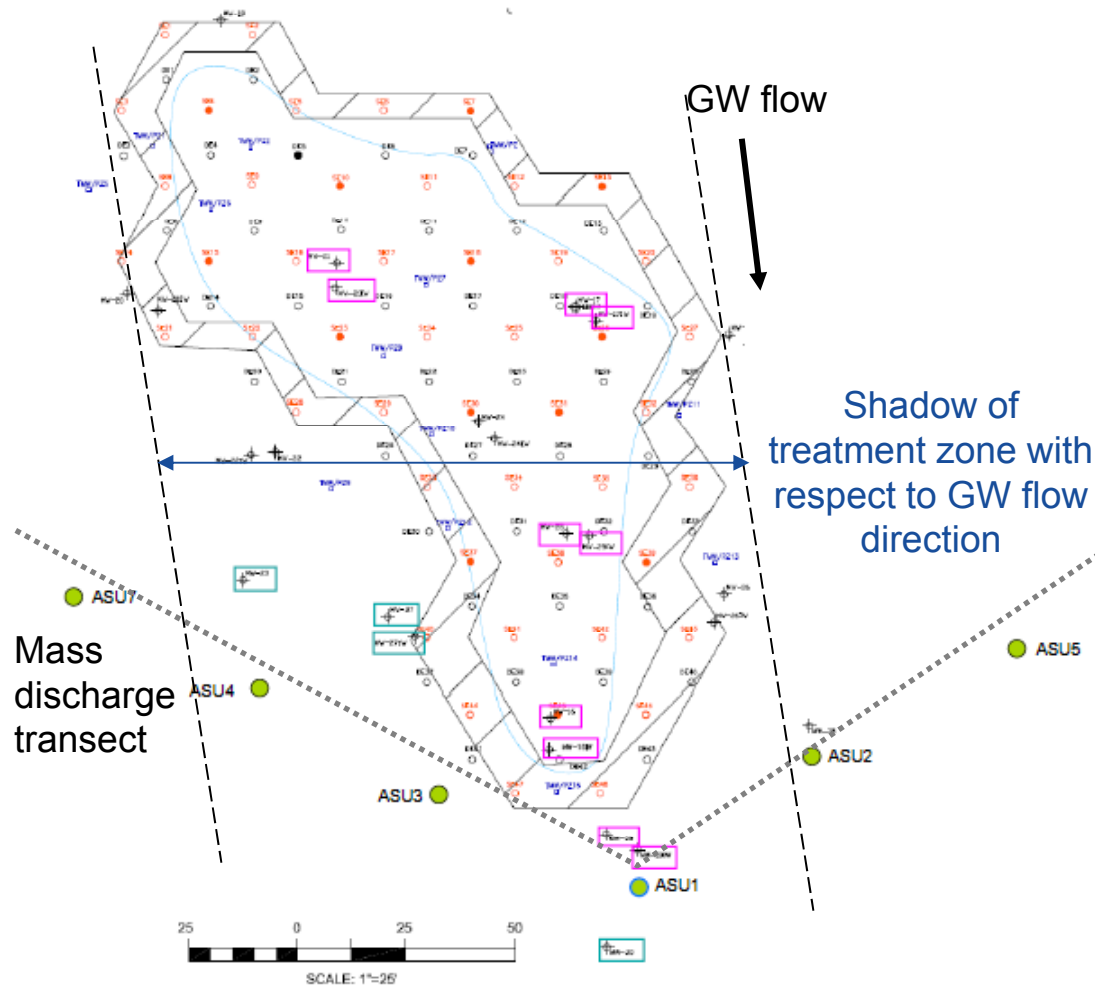
Camp Lejeune,
Jacksonville, NC

Hunter Army Airfield,
Savannah, GA

Hunter Army Airfield

Field Data Collection Approach

Supplemental data collection emphasizes **post-treatment groundwater quality** and **quantification of mass discharge** to the aquifer



Site Characteristics

Site ID	Technology	Geology at This Site is Most Like This Conceptual Scenario ¹	Number of Permanent Monitoring Wells	Type of Chemicals Treated (C-chlorinated solvents, P-petroleum hydrocarbons, W-Wood-treating, O-other)	Size of Target Treatment Area [ft ²]	Thickness of Target Treatment Interval [ft]	Depth to Water [ft]
Hunter Army Airfield Former Pumphouse #2	ERH	A	12	P, O	30,000	8	13
Air Force Plant 4 Bldg. 181	ERH	B	21	C	21,780	37	30
NAS Building 5, Site 5-1	ERH	C	15	C	14,520	20	6
EDGY Area 3	ERH	C	17	C, P	18,200	30	N/A
Site 89	ERH	C	26	C	15,873	21	5

¹Scenario Descriptors (for the target treatment zone)

A - relatively homogeneous and permeable unconsolidated sediments (sands, etc.)

B - largely impermeable sediments with interbedded layers of higher permeable material

C - largely permeable sediments with interbedded lenses of low permeable material

D - Competent, but fractured bedrock

E - Weathered Bedrock

ERH - Electrical resistance heating



Mass Discharge Sampling

Site ID	Number of Transect Sampling Locations	Transect Length (ft)	Vertical Sampling Interval (ft bgs)	Number of Depth- Specific GW Samples	Number of Aquifer Specific-Capacity Tests
Hunter Army Airfield Former Pumphouse #2	10	400	12 - 22	48	47
Air Force Plant 4 Bldg 181	10	170	29 - 35	13	9
NAS Site 5-1, Bldg. 5	7	115	6.5 - 21	39	39
Site 89	7	255	3 - 40	78	62
EGDY Area 3*	N/A	N/A	N/A	N/A	N/A

ft - Feet

bgs – Below ground surface

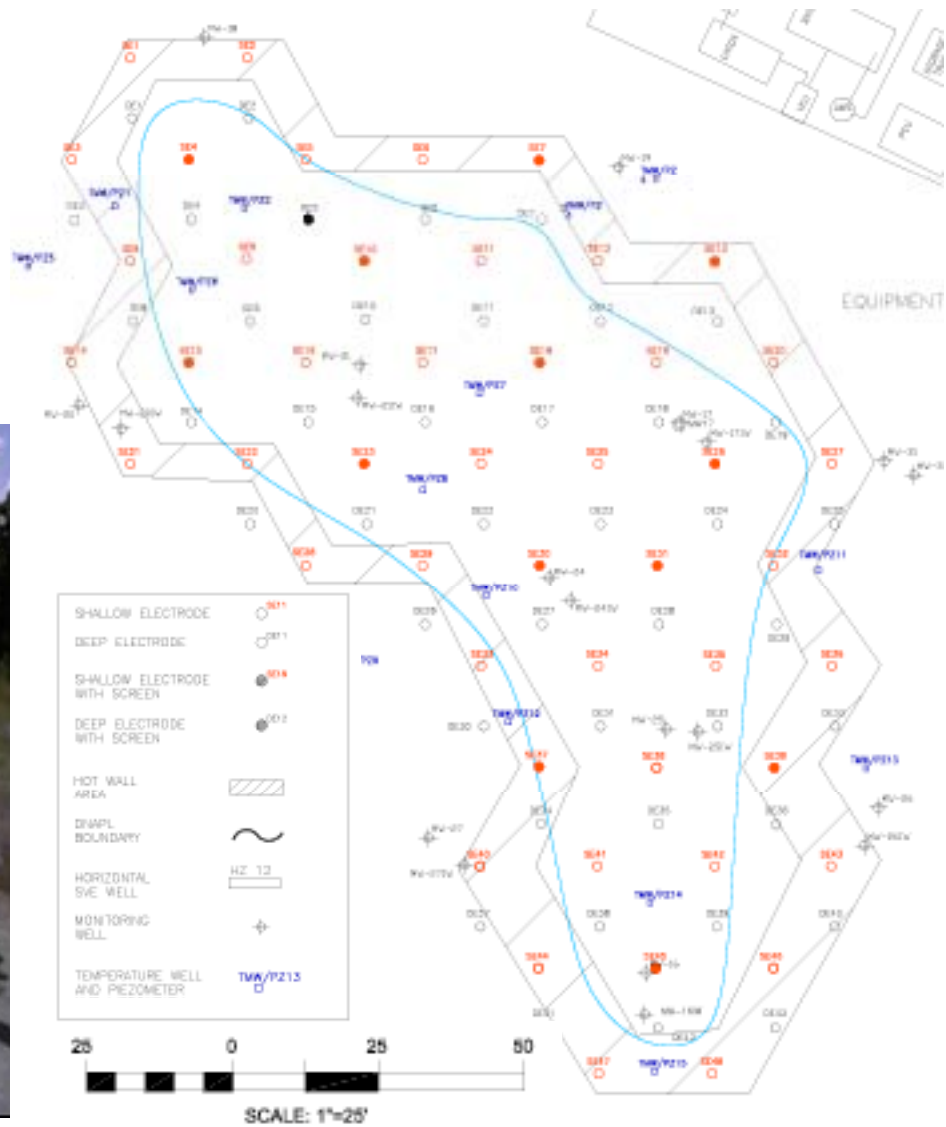
N/A – Not applicable to this site –

Note: All analysis were performed via groundwater samples from permanent monitoring wells collected by the Corp of Engineers and were sent directly to ASU for analysis. Analyses were performed pre-, during, and post-treatment to gauge how contaminant flux changed while treatment was occurring.

Example 1

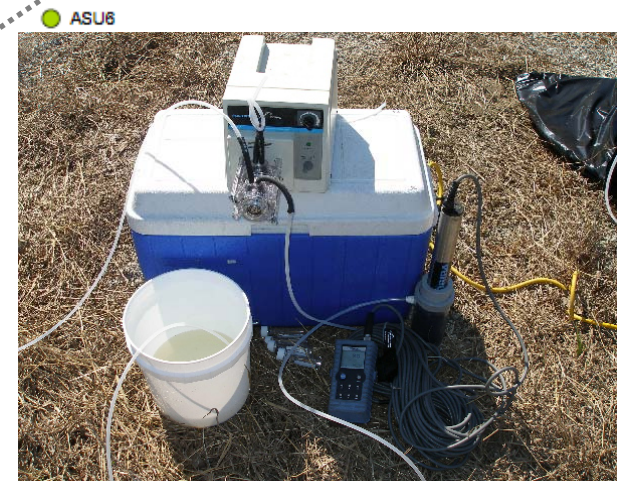
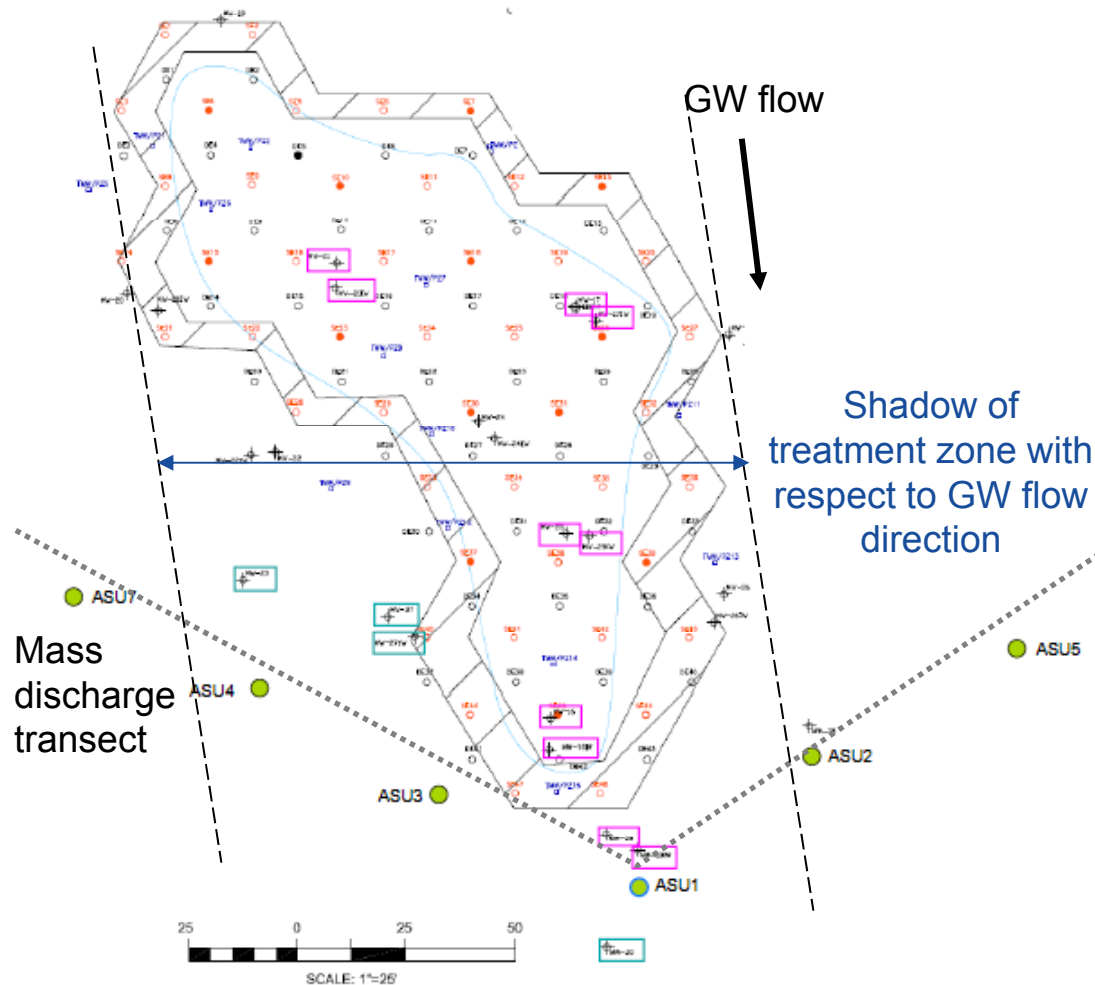
Camp Lejeune

- ERH Treatment 9/03 - 5/04
- DNAPL source
- 43 deep/48 shallow electrodes



Example 1: Sampling Locations

Supplemental data collection emphasizes post-treatment groundwater quality and quantification of mass discharge to the aquifer



Example 1 – Field Work

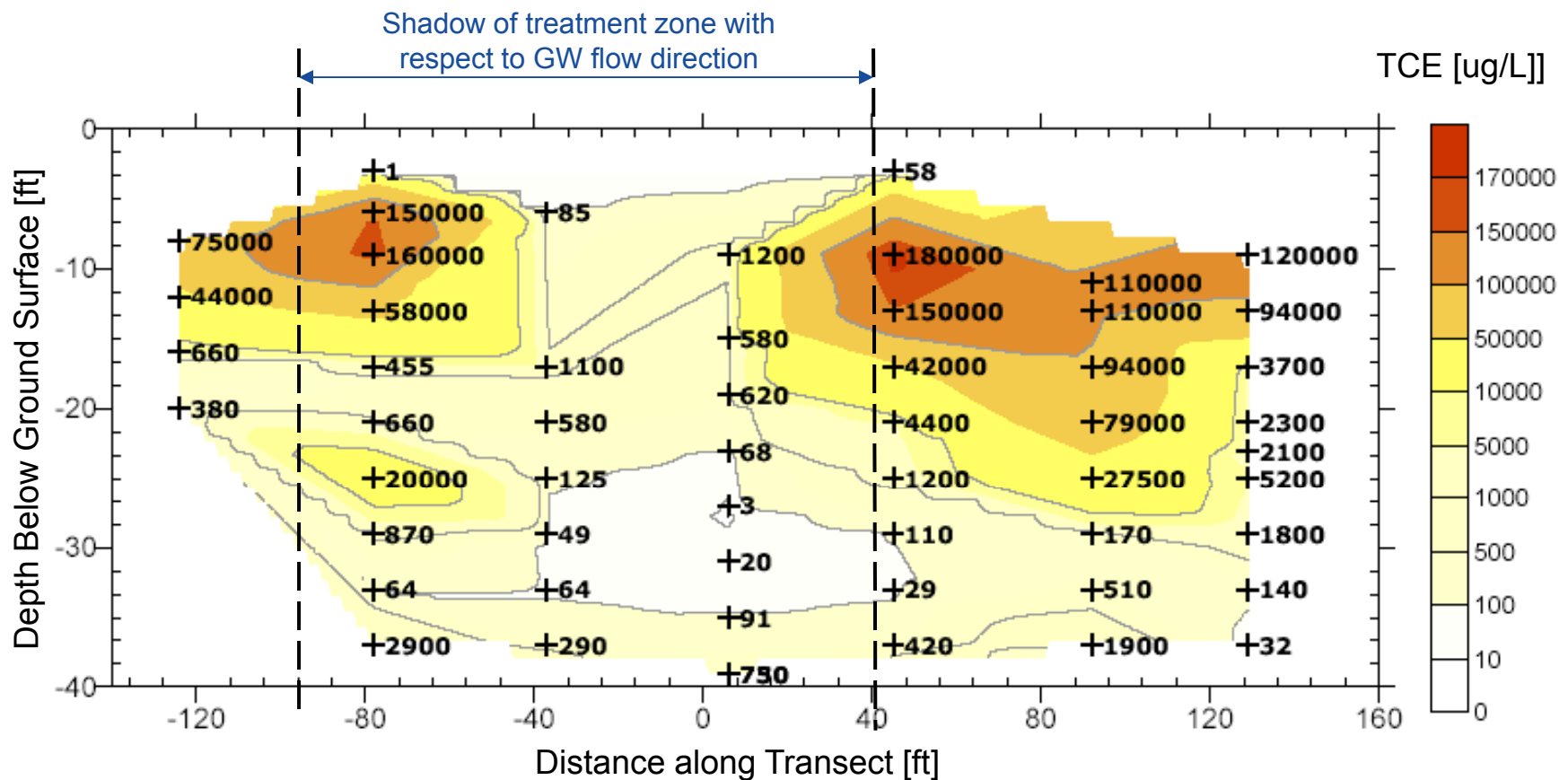
Activities at Camp Lejeune:

- Generic Demo Plan submitted Sept. 2005
- Site-specific Demo Plan Feb. 2006
- Field Activities 2/23/06 - 3/3/06
- 60+ hydraulic conductivity tests performed in 14 wells at 8 locations
- Continuous soil core collected at transect location
- 26 groundwater samples collected from 26 wells at 16 locations
- 78 depth-specific groundwater samples collected from 7 direct-push locations; aquifer characterization mini-pump tests performed at each depth
- pH, EC, Temp., DO, ORP, PCA, TCA, PCE, TCE, DCE isomers, VC



Concentration Transect

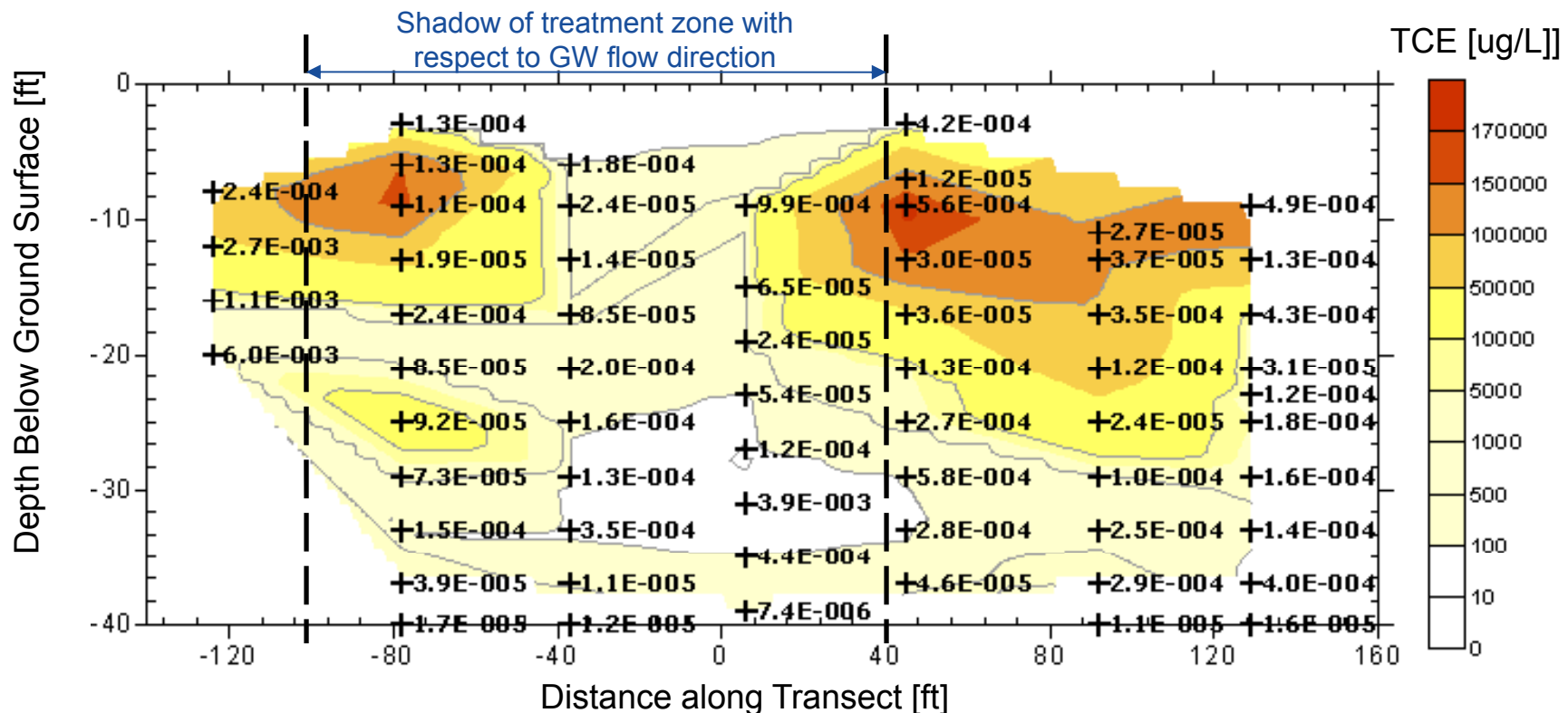
Camp Lejeune: TCE concentrations measured along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone.



Estimating Mass Discharge

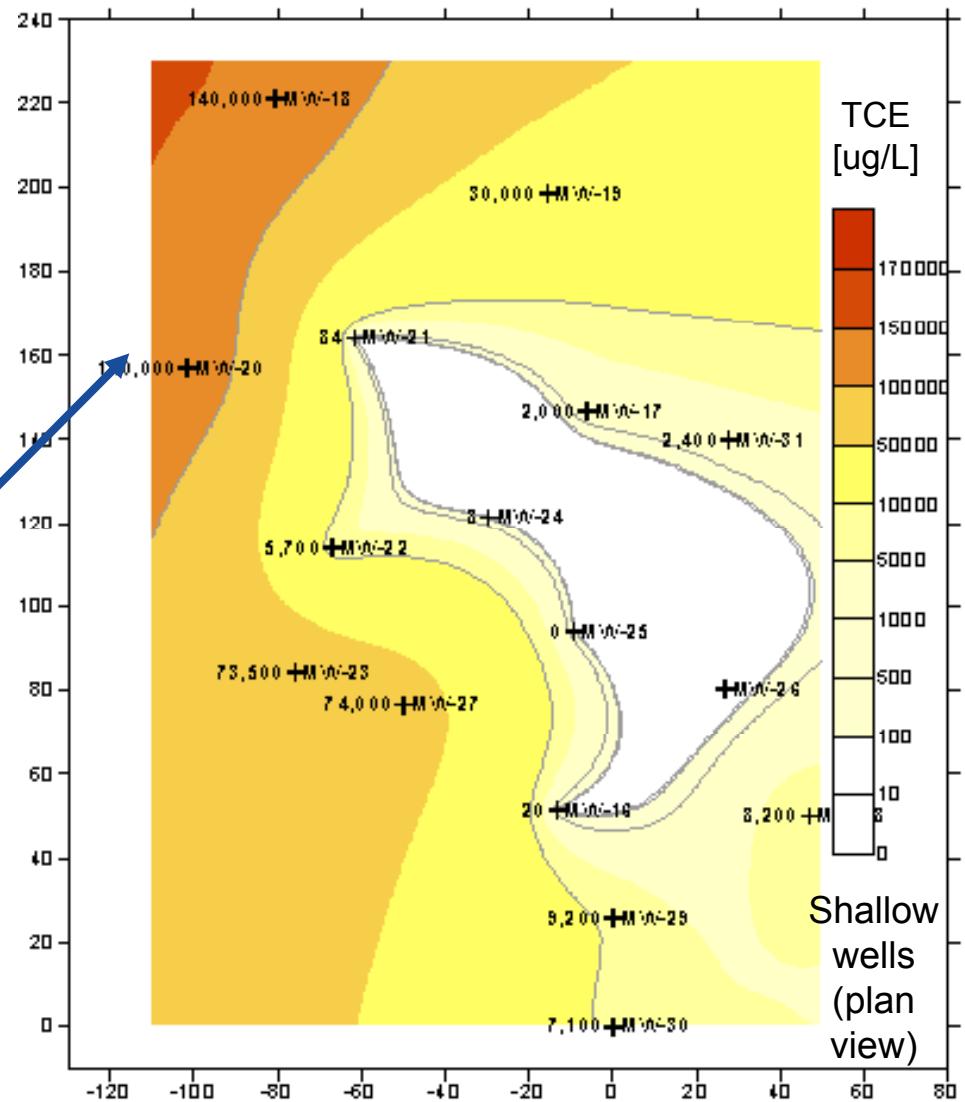
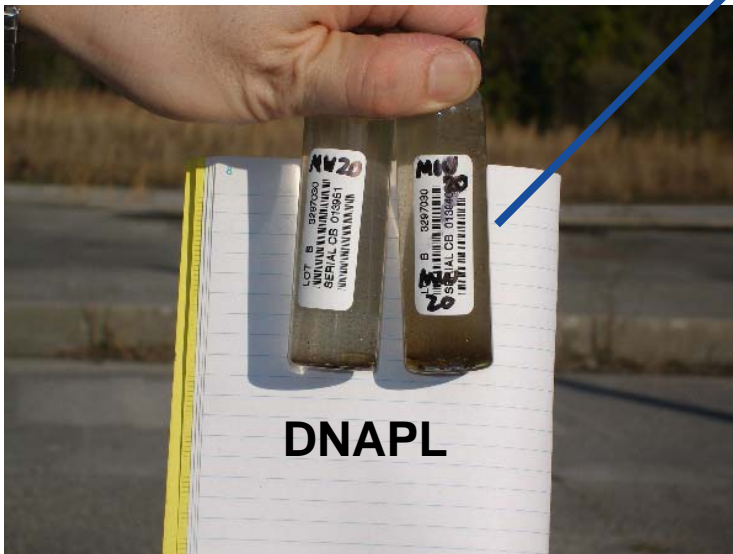
Data Presentation: hydraulic conductivities [cm/s] posted on top of TCE concentration contours [ug/L] along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone

Mass Discharge Calculation: estimated to be about 30 kg/y using the ESTCP-sponsored Mass Flux Toolkit Software from GSI



Example 1 - Conclusion

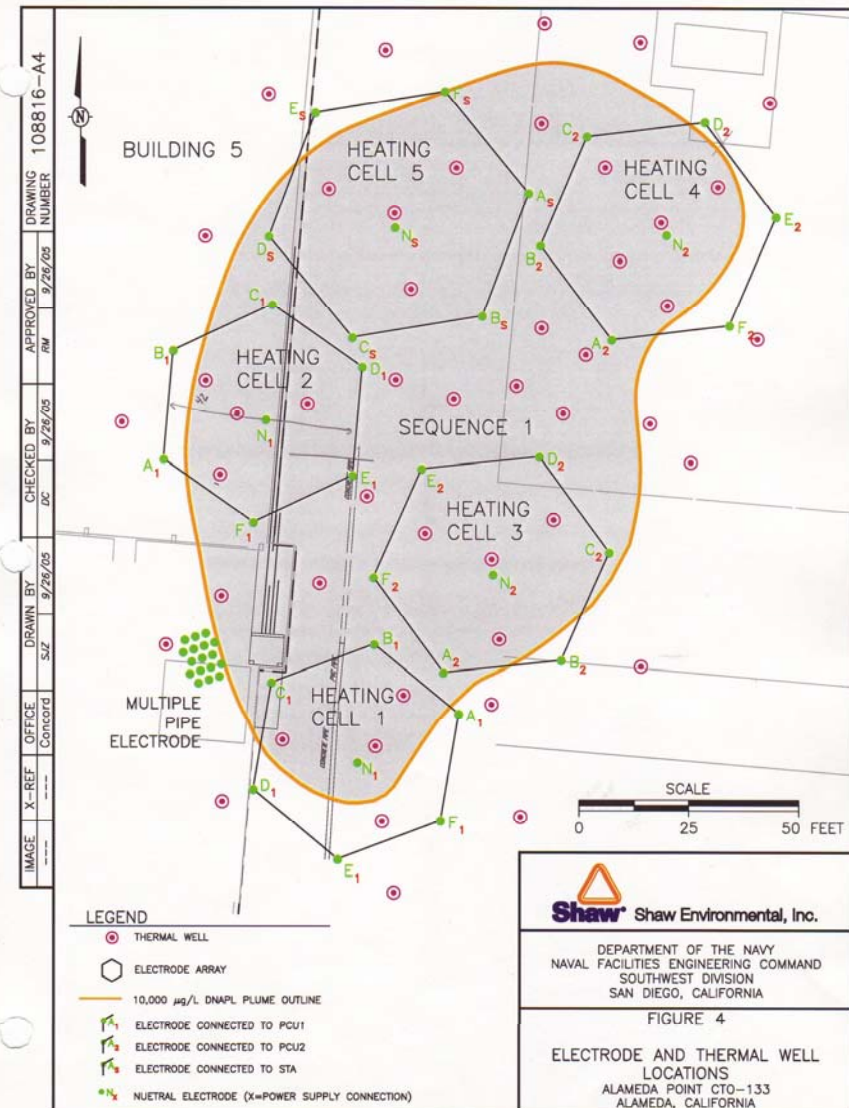
It is difficult to determine treatment effectiveness at this site because impacts from DNAPL residuals outside of the treatment zone (that were not fully-delineated prior to the ERH design and application) are masking the treatment effect.



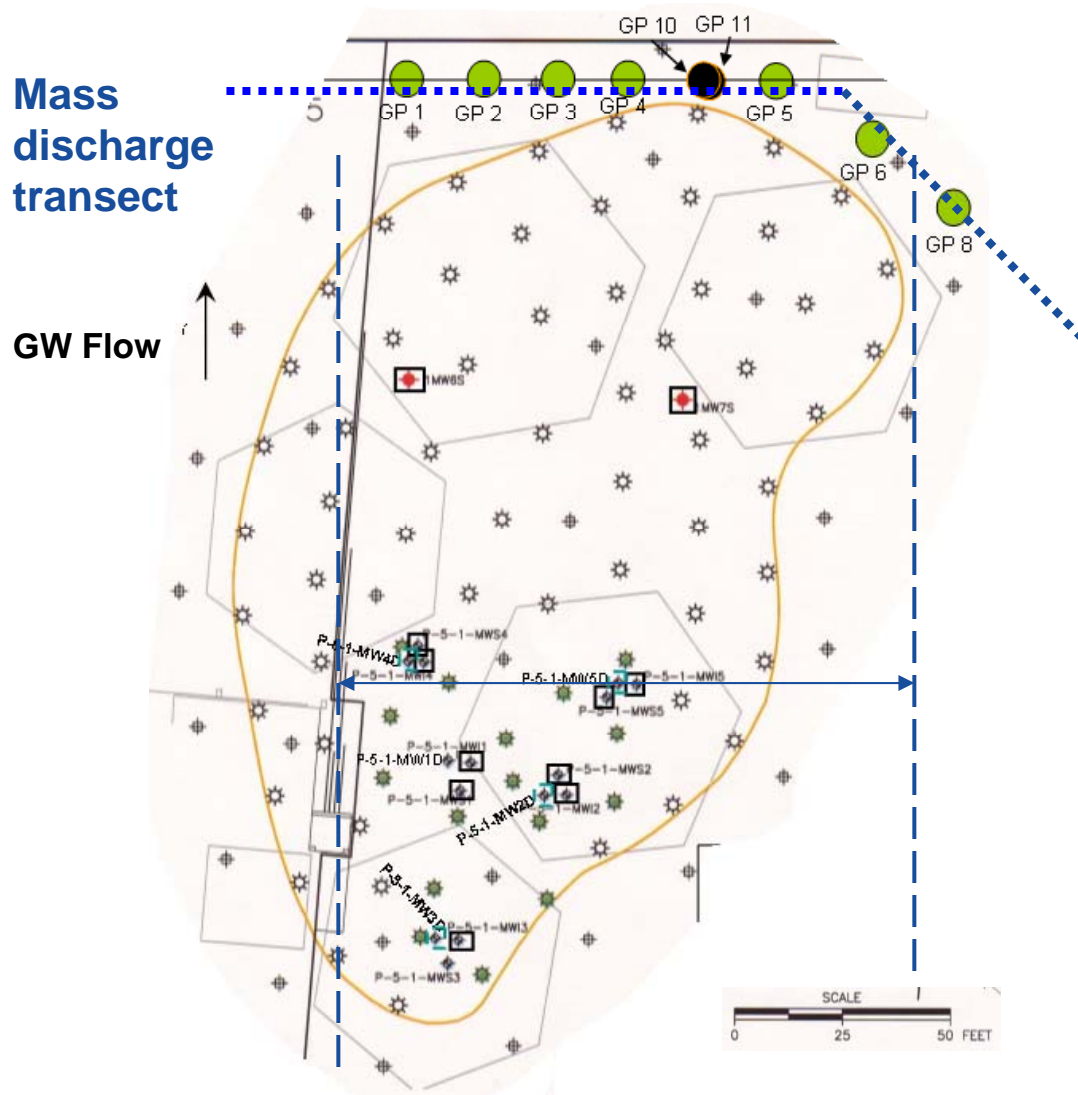
Example 2

NAS Alameda

- ERH Treatment 7/04 - 11/04
- DNAPL source
- 35 Energy delivery points with 4 sheet piles making-up an electrode



NAS Alameda ERH System Layout



Example 2 – Field Work

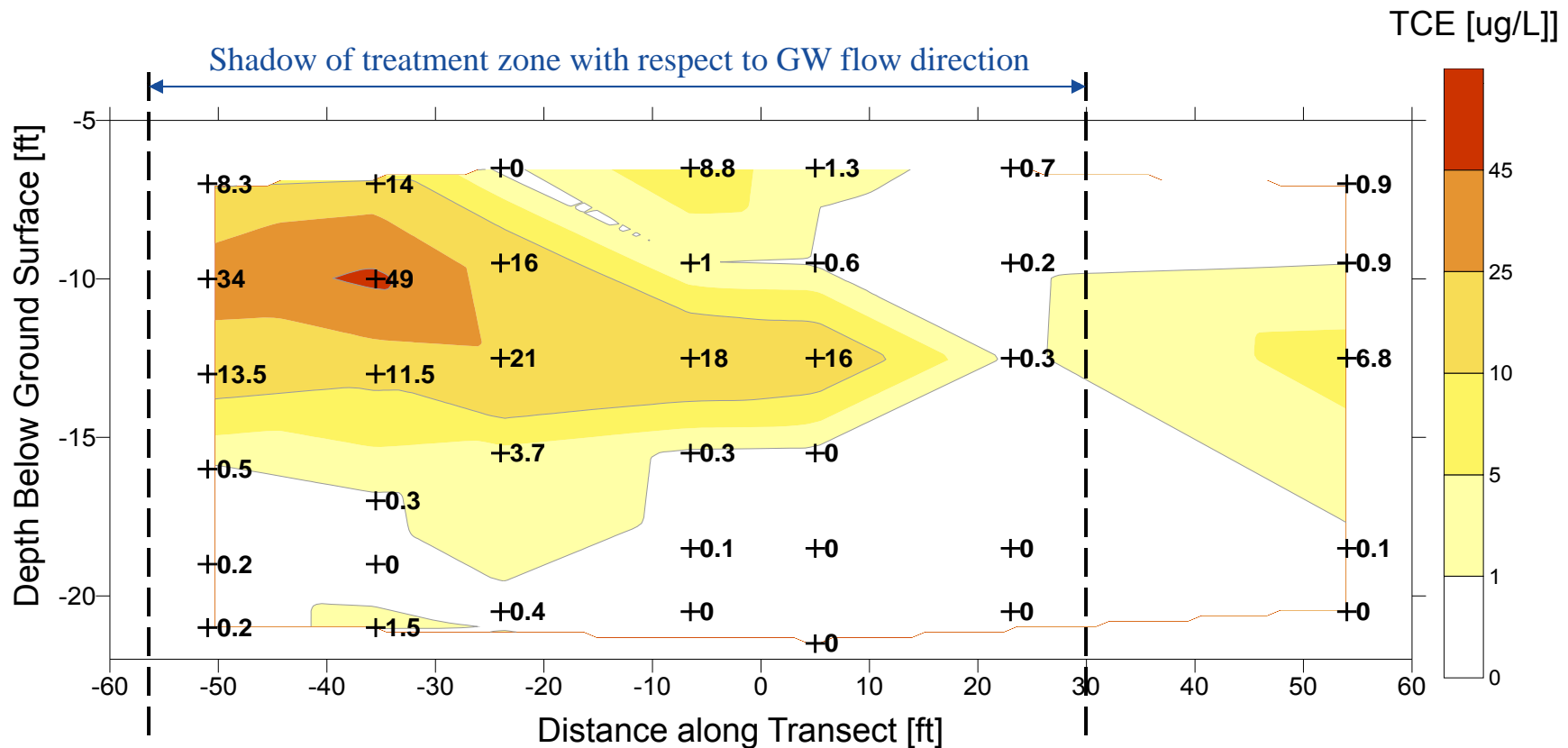
Activities at NAS Alameda:

- Generic Demo Plan submitted Sept. 2005
- Site-specific Demo Plan May 2006
- Field Activities 6/1/06 – 6/9/06
- 40+ hydraulic conductivity tests performed in
- 2 continuous soil core collected at transect location
- 11 groundwater samples collected from 11 wells at 7 locations
- 29 depth-specific groundwater samples collected from 7 direct-push locations; aquifer characterization mini-pump tests performed at each depth
- pH, EC, Temp., DO, ORP, TCA, PCE, TCE, DCA, DCE isomers, VC



Concentration Transect

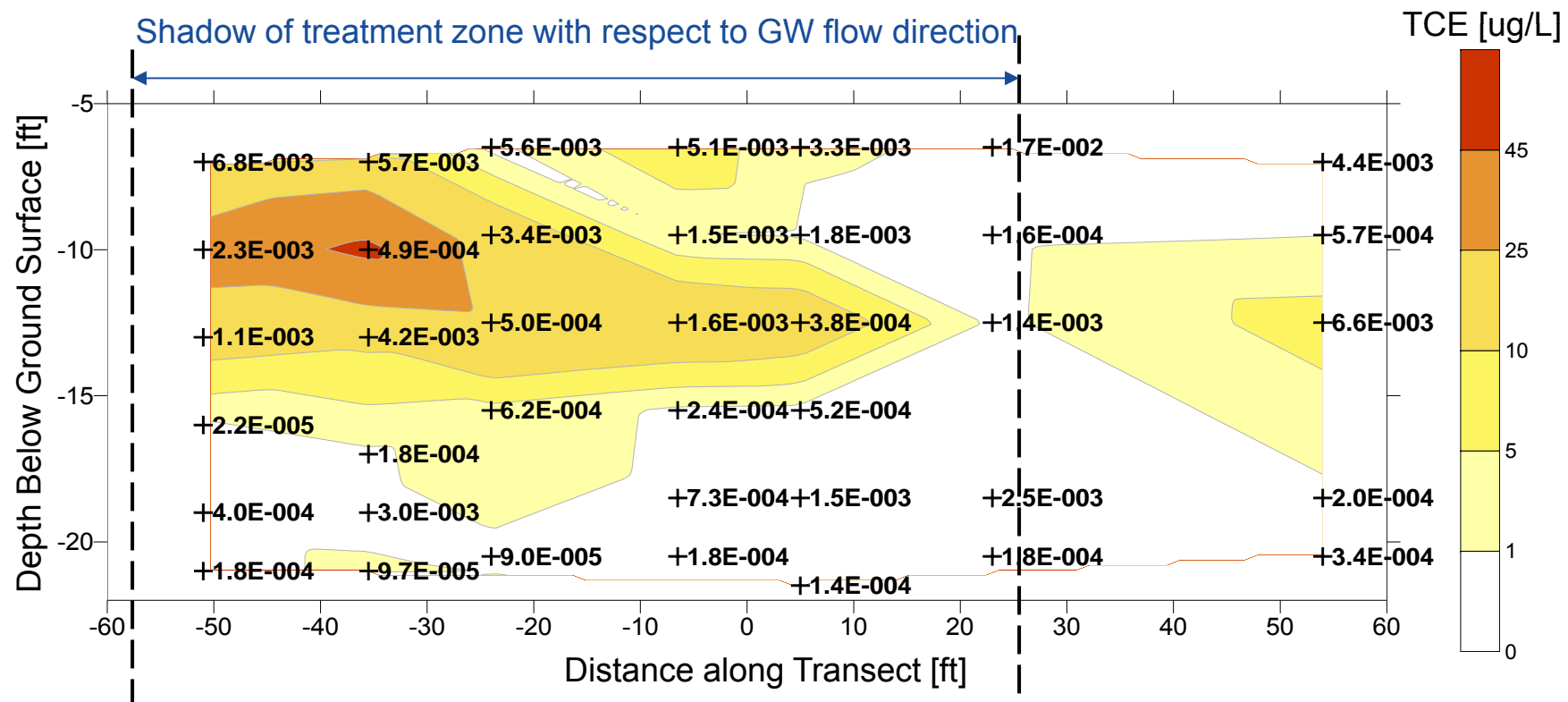
NAS Alameda: TCE concentrations measured along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone.



Estimating Mass Discharge

Data Presentation: hydraulic conductivities [cm/s] posted on top of TCE concentration contours [ug/L] as measured along the transect perpendicular to groundwater flow on the down-gradient edge of the source zone

Mass Discharge Calculation: estimated to be about $5.72\text{E-}03$ kg/y using the ESTCP-sponsored Mass Flux Toolkit Software from GSI



Example 2 - Conclusion

ERH treatment resulted in a significant reduction in contaminant concentrations throughout the 20 ft depth of treatment. Monitoring well concentrations for TCE ranged from 80 to 1 ug/L, while the direct push concentrations for TCE ranged from 49 ug/L to non-detect. Pre-treatment concentrations were in the range of 1,000 – 10,000 ug/L before full-scale treatment.



Summary of Mass Discharge Results

Site	Contaminant	Pre-treatment Discharge (kg/y) ¹	Post-treatment Mass Discharge (kg/y) ²	Post-treatment Mass Discharge per Linear Foot (kg/y/ft)
Hunter Army Airfield Former Pumphouse 2*	Total Contaminant Flux	5.2×10^1	1.9×10^{-1}	1.1×10^{-3}
Air Force Plant 4 Bldg 181**		6.0×10^1	2.1×10^1	1.4×10^{-1}
			4.9	3.4×10^{-2}
NAS Alameda Site 5-1, Bldg. 5*		4.9×10^1	1.3×10^{-1}	9.6×10^{-4}
Camp LeJeune Site 89*		6.8×10^2	8.2×10^1	5.5×10^{-1}
Ft. Lewis EGDY Area 3***		3.2×10^1	2.1	1.9×10^{-2}

Notes:

1 Mass discharge calculations were based on monitoring well data from the documentation.

2 Mass discharge calculations were based on discrete-depth sampling data, or a combination of discrete-depth sampling data and monitoring well data.

* Mass discharge calculations were base on discrete-depth sampling data only.

** Mass discharge calculations were performed for discrete-depth sampling data only and discrete-depth sampling data with monitoring well data.

*** Mass discharge calculations were based on monitoring well data analyzed by ASU personnel.

Post-Treatment Reductions

Site No.	Heating Technology	Generalized Scenario/Site	Dissolved Groundwater Concentration Reduction	Mass Discharge Reduction				
				<10x	10x	100x	1000x	>1000x
1	ERH	Generalized Scenario A ^(SDC)	10x			x		
2	ERH	Generalized Scenario B ⁺ ^(SDC)	<10x	x	x			
3	ERH	Generalized Scenario C	10x		x			
4	ERH	Generalized Scenario C* ^(SDC)	>10x to <100x		x			
5	ERH	Generalized Scenario C [^]	<10x	x				
6	ERH	Generalized Scenario C [^]	<10x	x		x		
7	ERH	Generalized Scenario C	<10x				x	
8	ERH	Generalized Scenario C ^(SDC)	10x		x			
9	ERH	Generalized Scenario C ^(SDC)	100x			x		
10	ERH	Generalized Scenario C	1000x		x			
11	SEE	Generalized Scenario C	100x			x		
12	SEE	Generalized Scenario C	10x	x				
13	SEE	Generalized Scenario C [^]	10000x				x	x
14	SEE	Generalized Scenario D*	<10x	x				

* Pilot application appeared to encompass the entire source zone based on documentation reviewed.

+ Mass discharge assessment involved two calculations using first only the post-treatment field investigation data and then the post-treatment field investigation data supplemented with data from a set of monitoring wells that were directly in line with the field investigation transect.

[^] Site used two different vertical intervals to calculate mass discharge: 1) Only shallow geology and 2) shallow and deep geology.

SDC – supplemental data collection site for this project

Mass Discharge Summary – All Sites

Site No.	Heating Technology	Site	Contaminant	Pre-treatment Discharge (kg/y)	Post-treatment Discharge (kg/y)
1	ERH	Generalized Scenario A	Total Contaminant Mass Discharge (sum of all components)	5.2×10^1	1.9×10^{-1}
2	ERH	Generalized Scenario B		6.0×10^1	2.1×10^1
					4.9
3	ERH	Generalized Scenario C		4.0×10^{-1}	3.1×10^{-2}
4	ERH	Generalized Scenario C		6.8×10^2	8.2×10^1
5	ERH	Generalized Scenario C		1.7	6.0×10^{-1}
				2.4	9.7×10^{-1}
6	ERH	Generalized Scenario C		9.4	2.7×10^{-2}
				4.9	1.6
7	ERH	Generalized Scenario C		9.3	1.7×10^{-2}
				7.4	1.6×10^{-2}

Mass Discharge Summary – All Sites

Site No.	Heating Technology	Site	Contaminant	Pre-treatment Discharge (kg/yr)	Post-treatment Discharge (kg/yr)
8	ERH	Generalized Scenario C	Total Contaminant Mass Discharge (sum of all components)	3.2×10^1	2.1
9	ERH	Generalized Scenario C		4.9×10^1	1.3×10^{-1}
10	ERH	Generalized Scenario C		1.2	5.4×10^{-2}
11	SEE	Generalized Scenario C		4.6	7.3×10^{-2}
12	SEE	Generalized Scenario C		1.3	2.8
13	SEE	Generalized Scenario C		1.9×10^{-2}	1.8×10^{-7}
				2.9×10^{-4}	1.1×10^{-7}
14	SEE	Generalized Scenario D		9.7×10^{-2}	6.1×10^{-2}



Key Observations

- **Data Collection:**

- ◆ 182 applications conducted between 1988 and 2007 were identified and reviewed, including
 - 87 electrical resistance heating,
 - 46 steam-based heating,
 - 26 conductive heating, and
 - 23 other heating technology applications.
- ◆ This information indicates that a significant number of applications have occurred and it reflects the acceptance of in situ thermal technologies as viable source zone treatment options.



Key Observations

- Trends in Current Applications
 - ◆ Approximately half of the 182 applications have been implemented since 2000 and over half of those have been ERH systems.
 - ◆ ERH applications outnumber all other applications since 2000 by about a factor of three.
 - ◆ There appears to be a recent trend in the increasing use of conductive heating and decreasing use of steam-based heating.



Key Observations

- Operating Conditions
 - ◆ Steam and ERH systems are inherently limited to operating temperatures at about the atmospheric boiling point of water (100 C) or lower, and most systems operate close to that range.
 - ◆ Conductive heating is the only option for achieving significantly higher temperatures than that.



Key Observations

- Energy Delivery Design

- ◆ There appears convergence towards relatively closely-spaced energy delivery points in the design of ERH and conductive heating systems.
 - Spacing for most ERH and conductive energy delivery points was less than 20 ft (6 m).
 - Steam application well spacing was usually greater than 20 ft (6 m).



Key Observations

- Treatment Zone Size

- ◆ 117 of 121 treated areas were $<4 \times 10^4 \text{ ft}^2$ ($<4000 \text{ m}^2$ or an acre) and two-thirds of those were $<10^4 \text{ ft}^2$ ($<1000 \text{ m}^2$ or one-quarter acre treatment areas)
- ◆ It is also apparent that the spatial extents of many source zones are likely ill-defined prior to treatment.
- ◆ This results in under-sized target treatment zones, untreated source zone areas, and minimal beneficial impact to groundwater quality and mass discharge.



Key Observations

- Geologic Setting Effects
 - ◆ The effect of geologic setting on performance is difficult to discern in this data set.
 - Most treatment systems were installed in layered settings, characterized as either primarily fine-grained materials with higher permeability lenses (Generalized Scenario B) or primarily permeable materials with finer-grained lenses (Generalized Scenario C).



Key Observations

- Application Operating Times
 - ◆ Most applications (independent of specific technology) lasted less than 6 months
 - There was little documentation as to the criteria or rationale used to determine the duration of operation.
 - There was little indication that the duration of operation was linked to mass removal-, groundwater quality-, or soil concentration-based criteria.



Performance Expectations

- Supplemental data collection indicated that a 100x reduction was achievable if the source zone was adequately delineated and fully encompassed during treatment and if the system was operated for a sufficient period of time.
 - ◆ Reductions of less than 100x were seen if the system was not operated for a sufficient period of time, and at sites where the source zone was not fully encompassed a reduction of <10x was typical.
- For sites with a concentration reduction of 100x or more, the final groundwater concentrations could be less than 100 ug/L for individual constituents which then could correspond to a mass discharge of 1E-01 kg/y or less.



Correlations

- Mass discharge reduction to temperature
 - ◆ Available data suggests that achieving a target temperature is insufficient to achieve good clean-up, and that application duration, in combination with the treatment zone temperature and treatment zone size likely control the performance.



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ESTCP

Technology Transfer

Combined results from this project and vendor-authored/ASU-edited state-of-the-practice write-ups for key thermal treatment technologies in a users guide targeting program manager, consultant, and regulator audiences.

Thermal tech-transfer meeting in WA in early stages of the project.

Articles in press and under review in GWMR.



**State-of-the-Practice Overview
of the Use of In Situ Thermal
Technologies For
NAPL Source Zone Cleanup**



Jennifer Triplett Kingston ¹, Paul R. Dahlen, and Paul C. Johnson
Arizona State University

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Battelle Memorial Institute

With contributions from:

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Greg Smith (Thermal Remediation Services, Inc.)
Phil La Mori and Elgin Kirkland (FECC Corporation)

May 2009

¹ Now with Haley and Aldrich, Lenexa, Kansas

Acknowledgements

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- Shaw Environmental
- URS
- CES
- TRS
- Haley and Aldrich (M. Basel)
- ERM
- Army Corps of Engineers
- McMillian-McGee
- EPA
- Department of Defense – Military branches
- Department of Energy
- And the numerous consulting firms involved in thermal applications that helped us with documentation

The ASU and Battelle team would like to thank the following people for their help in accessing field sites:

- Ron Kenyon (Shaw)
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- Doug DeLong (Navy)
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- Rick Wice (Shaw)
- George Walters (AF)
- Randall McDaniel (Shaw)
- Algeana Stevenson (AF)
- Phil La Mori (BEM Systems)
- Mark Kershner (AF)
- Emile Pitre (USACE)
- Kira Lynch (USACE)

THERMAL TREATMENT TECHNOLOGIES: LESSONS LEARNED

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12:30 PM		Adjourn



Measuring and Modeling Thermal Treatment at Naval Air Warfare Center

Project # ER-200715

Professor Bernie Kueper
Department of Civil Engineering, Queen's University

C. Lebron, G. Heron, J. Lachance, D. Rodriguez, D.
Baston, A. Wemp, P. Lacombe, others. . .



Thermal Conductive Heating (TCH) in Fractured Rock

- Introduction to TCH
- TOPIC #1 - Influence of inflowing cold groundwater in fractures
- TOPIC #2 - Ability to observe boiling in rock matrix
- TOPIC #3 – NAWC Site pilot test results
- TOPIC #4 - Field parameters to measure

Thermal Conductive Heating

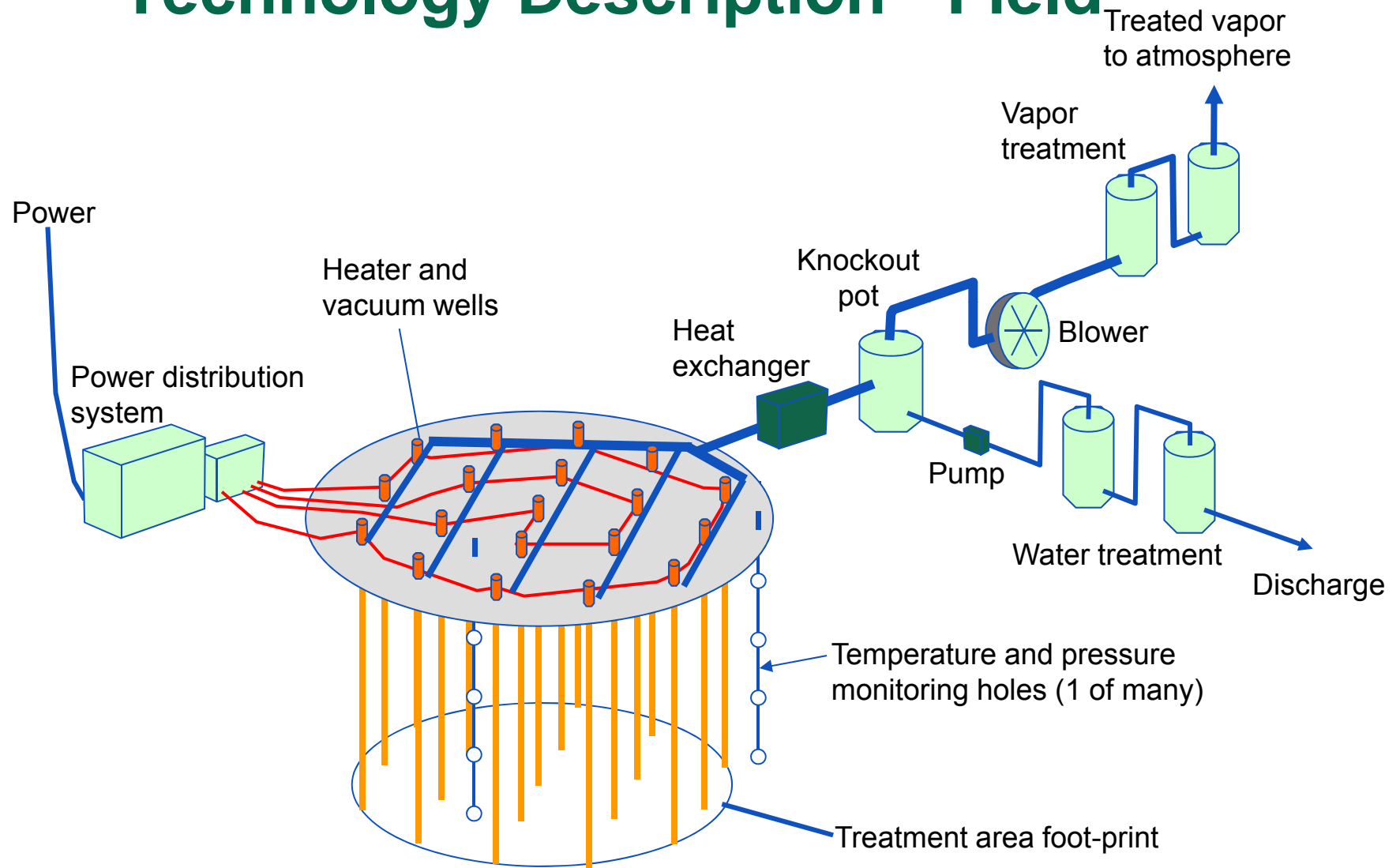
Thermal
Blanket

Thermal
Wells





Technology Description - Field



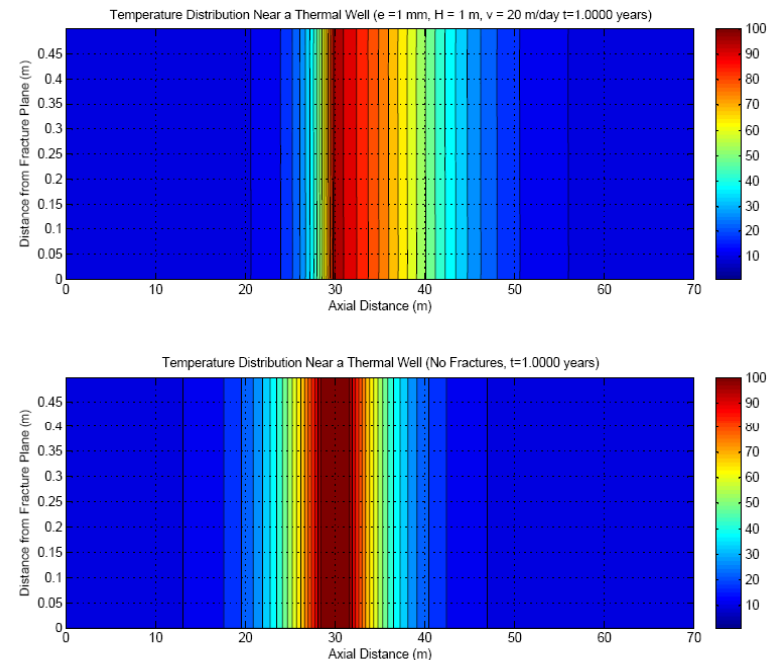
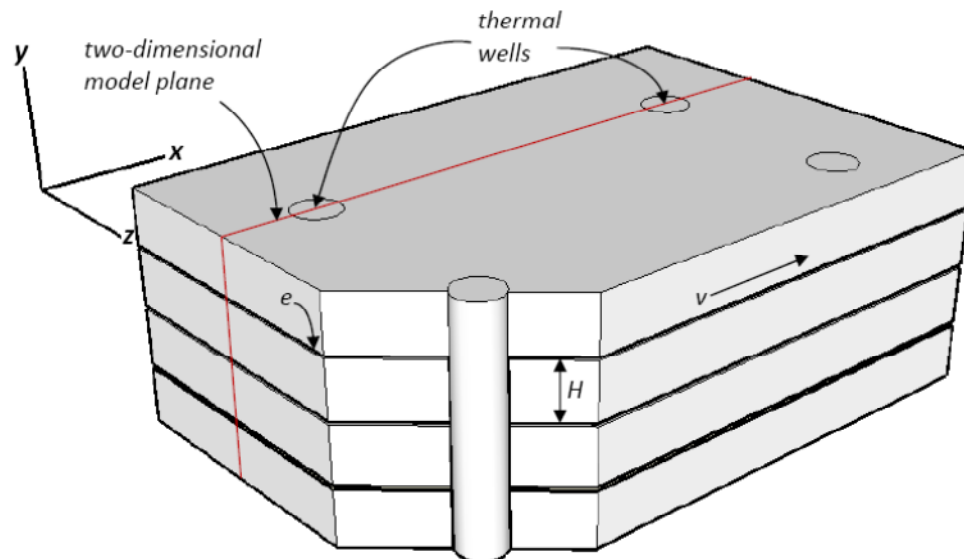
TCH Heaters



Protected by U.S. and International Patents

Compliments of Terratherm

TOPIC #1 - Assess influence of inflowing cold groundwater on ability to reach boiling in rock



Baston, D., Heron, G. and Kueper, B.H., 2007. Screening level modeling of thermal conductive heating in fractured rock. Proceedings, USEPA/NGWA Fractured Rock Conference, Portland, ME.

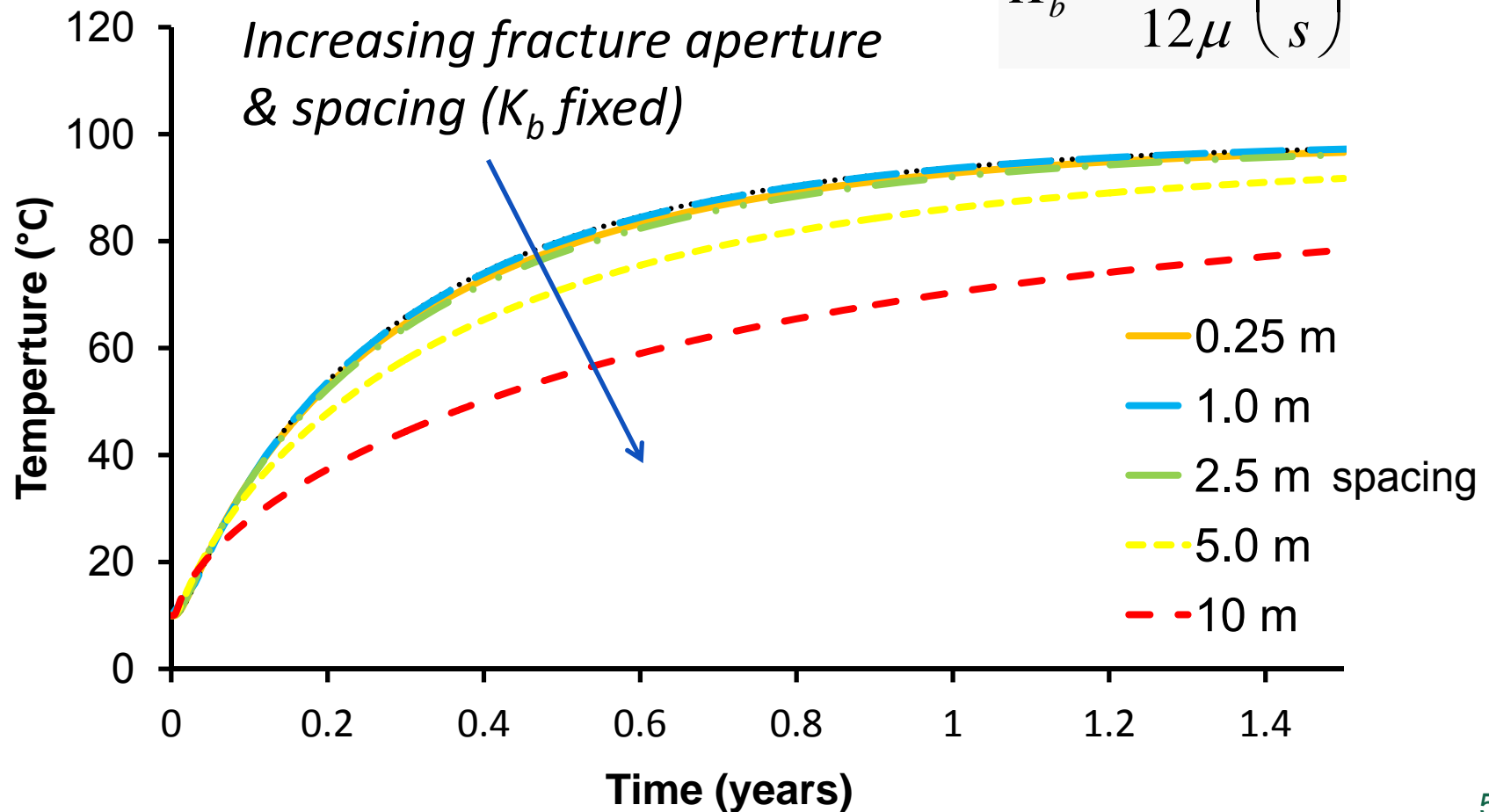
Baston, D.P. and Kueper, B.H., 2009. Thermal conductive heating in fractured bedrock: screening calculations to assess the effect of groundwater influx. *Advances in Water Resources*, 32, pp. 231-238.



Temperature Between Thermal Wells

($q = 33.7 \text{ L/m}^2\cdot\text{day}$)

$$K_b = \frac{e^2 \rho g}{12 \mu} \left(\frac{e}{s} \right)$$



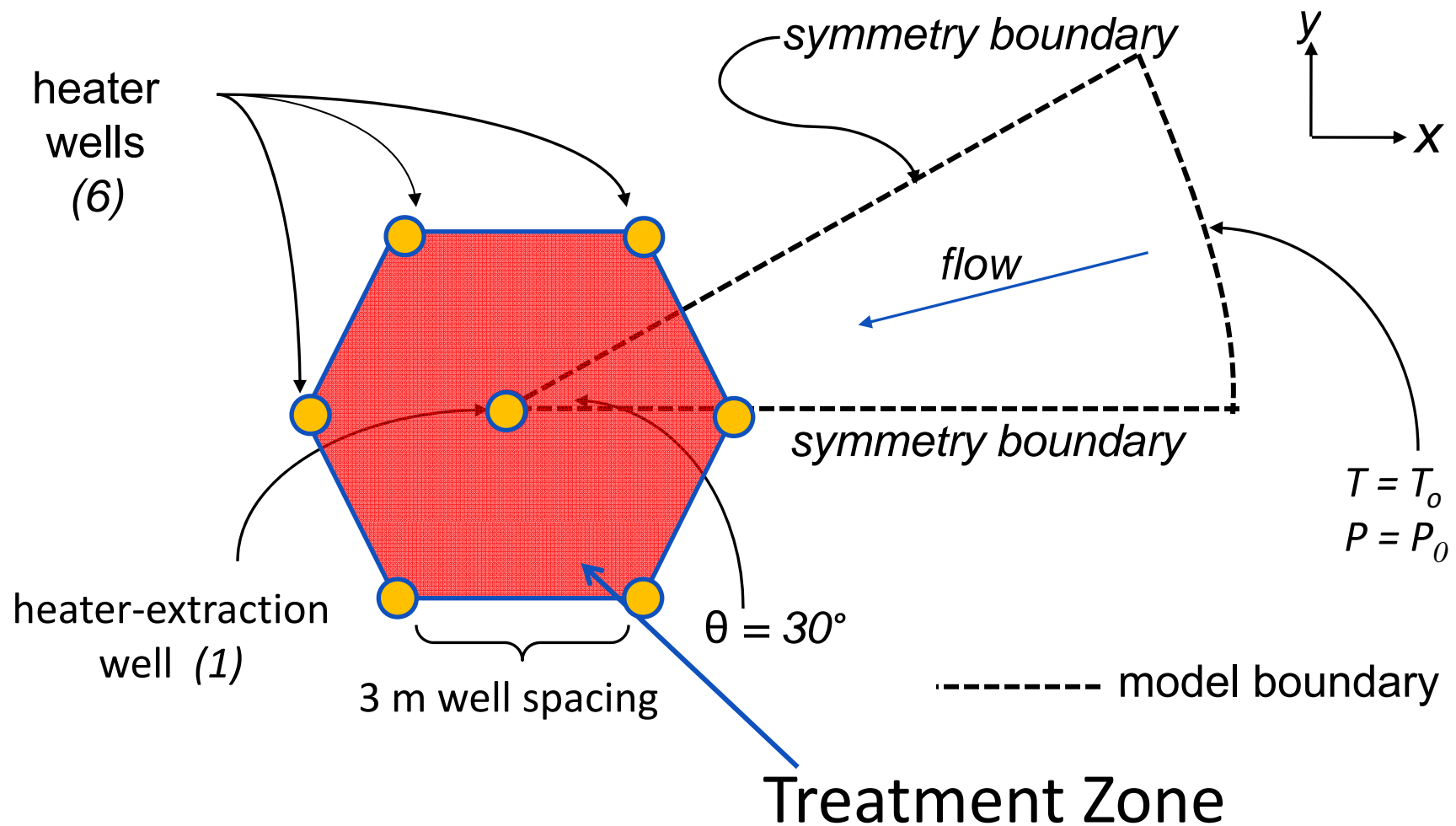


TOPIC #1 - Conclusions

- Inflowing cold groundwater can prolong time required to reach boiling in rock
- Site characterization should focus on
 - ◆ Bulk K of rock (hydraulic testing),
 - ◆ Fracture spacing (e.g., downhole televiewer),
 - ◆ Hydraulic gradient

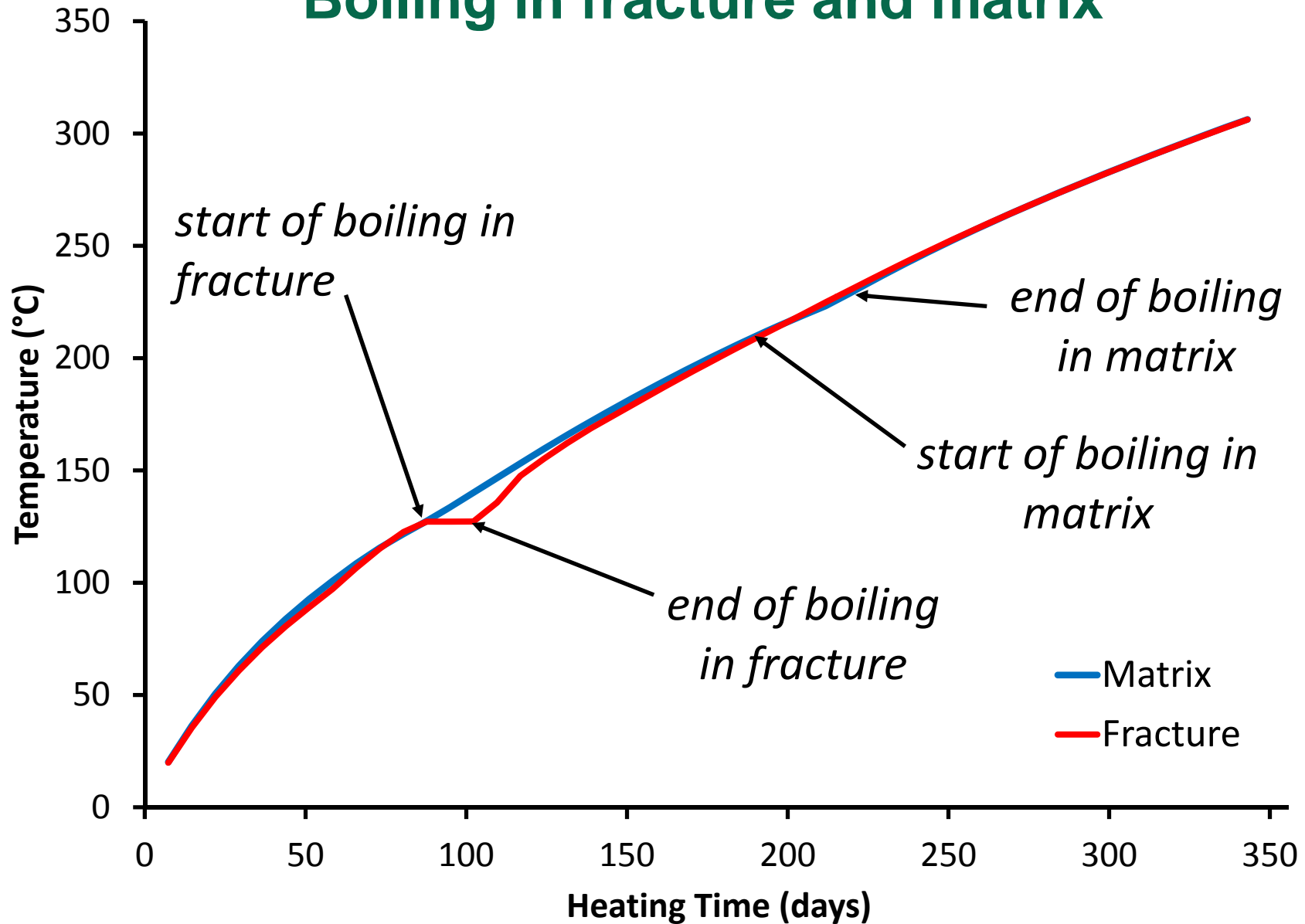


TOPIC #2 - Assess influence of rock properties on ability to reach boiling in rock matrix

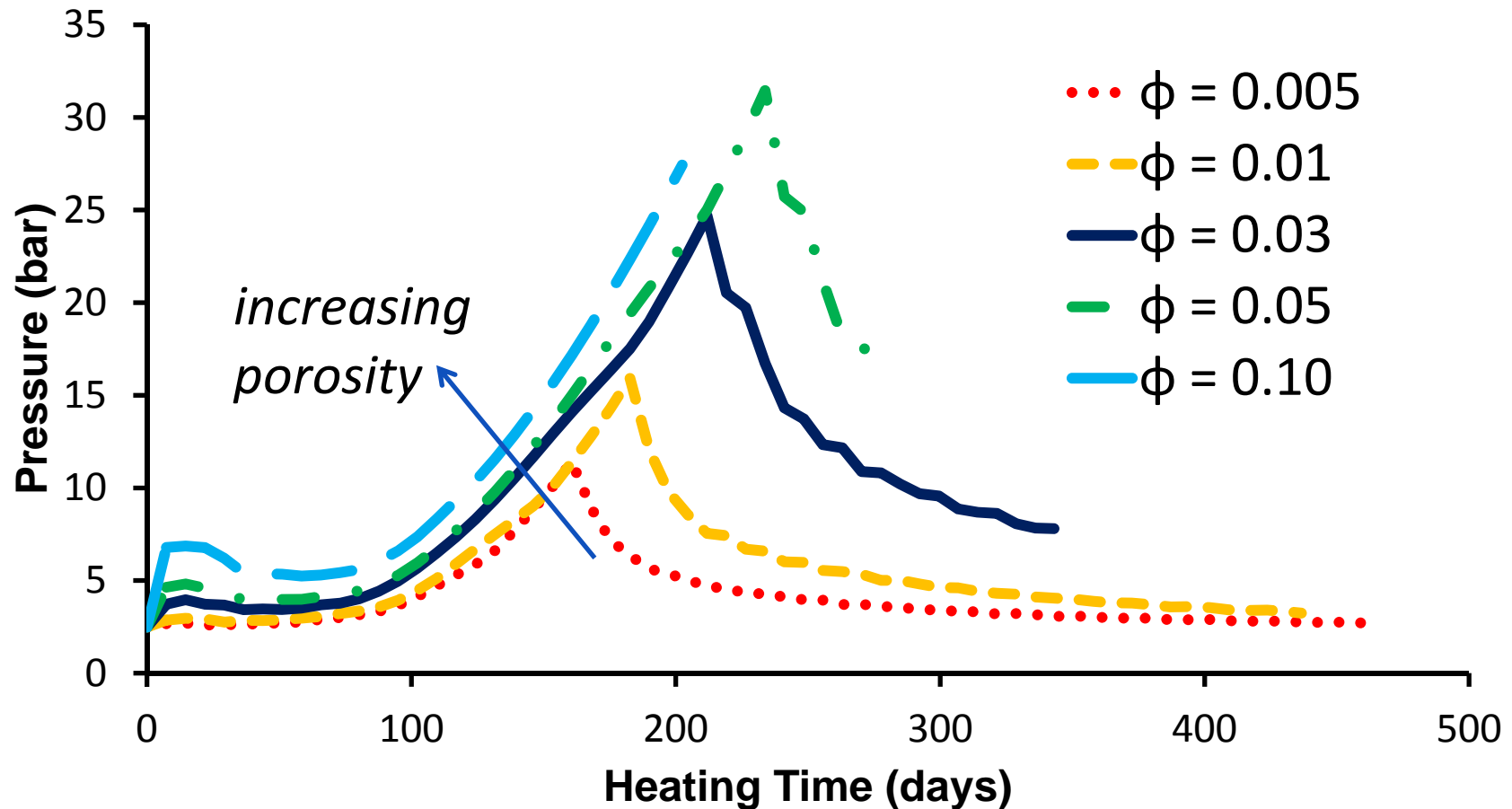




Boiling in fracture and matrix



Pressure spike in matrix corresponding to boiling



TOPIC #2 - Conclusions

- It may be difficult to monitor progress of heating in bedrock because of:
 - (i) Variability of boiling point in the rock matrix (T function of P)
 - (ii) Lack of well defined temperature plateau indicating boiling in matrix,
- Pressure monitoring may be beneficial

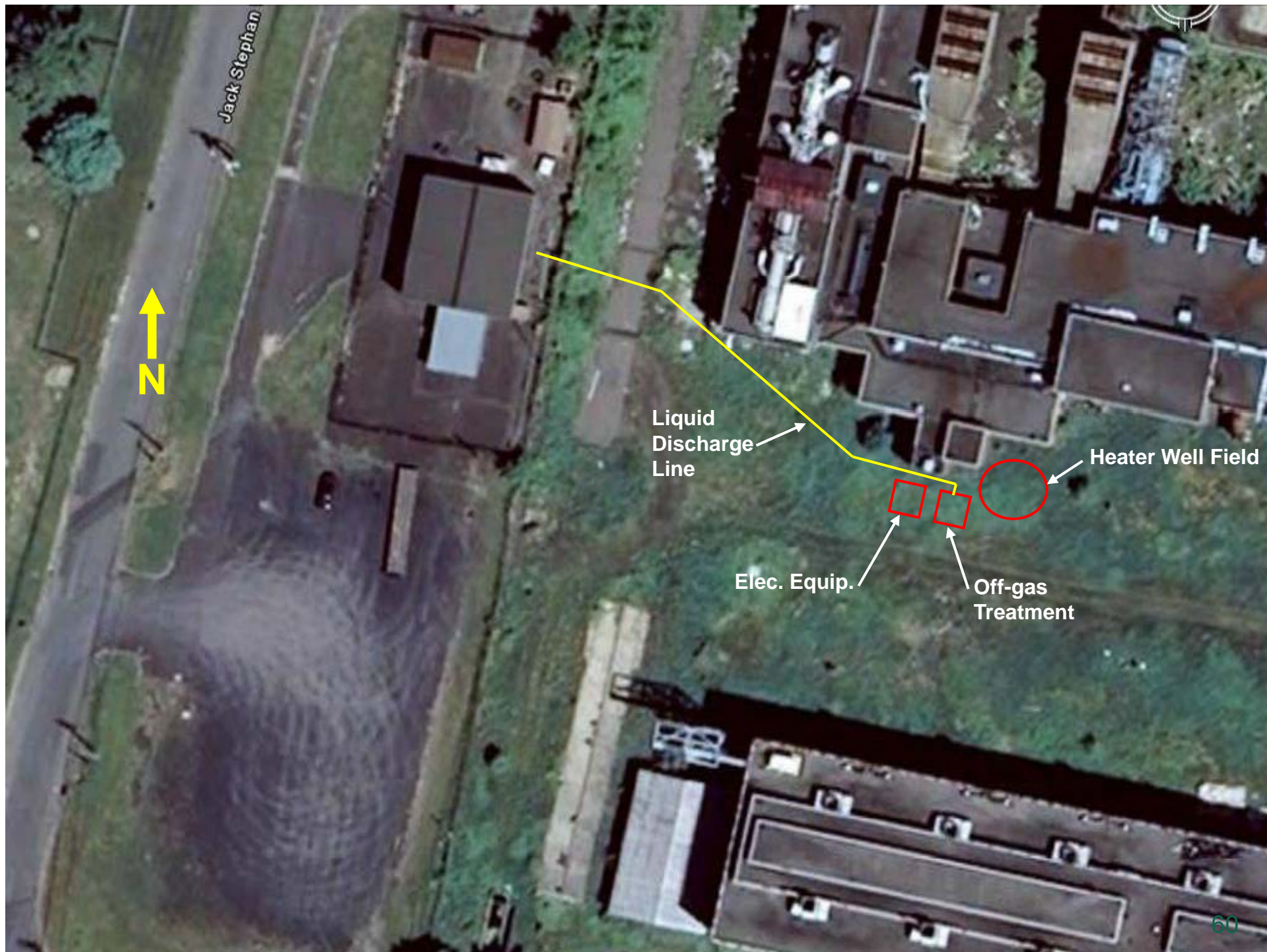
Baston, D.P., Falta, R.W. and Kueper, B.H., 2010. Numerical modeling of thermal conductive heating in bedrock. Journal of Ground Water.

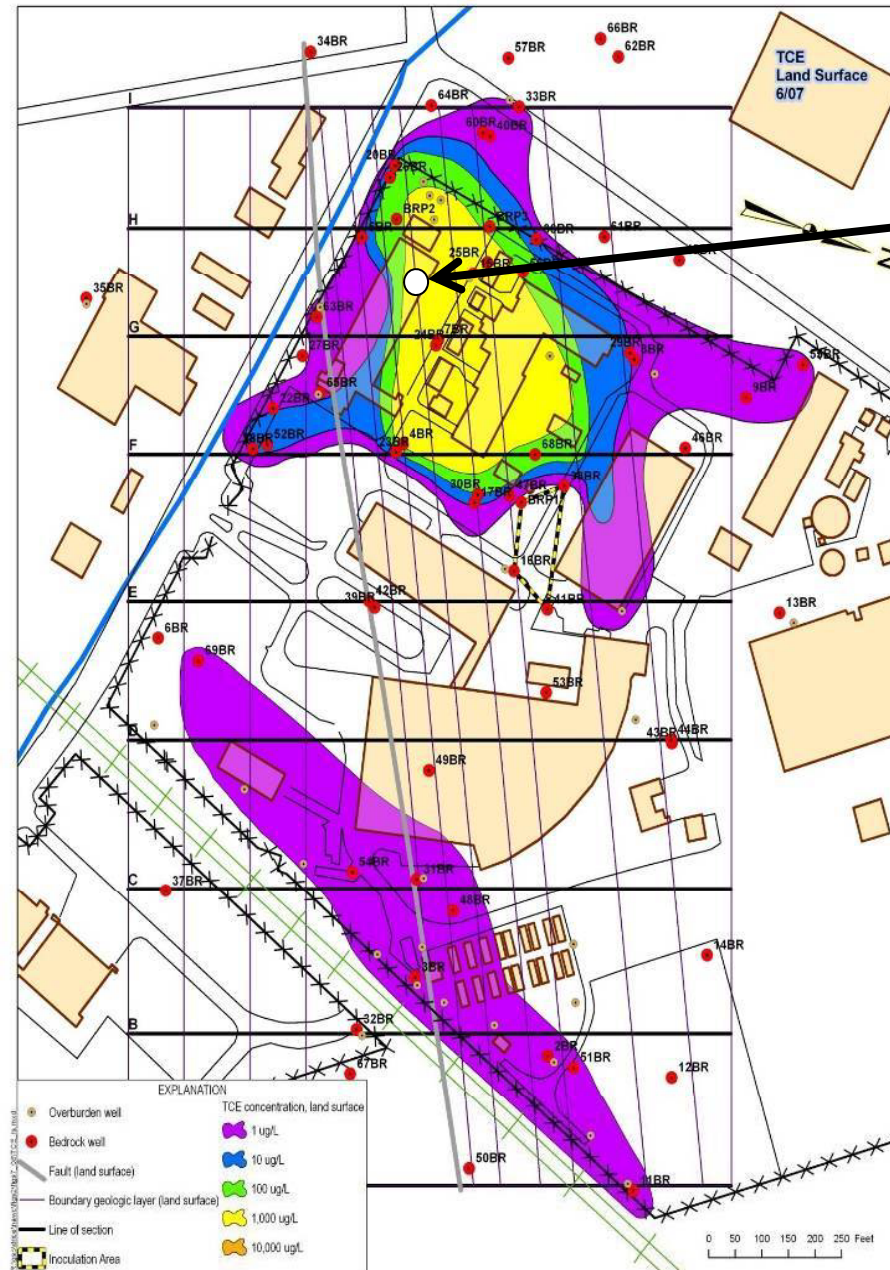
TOPIC #3 – NAWC Pilot Test



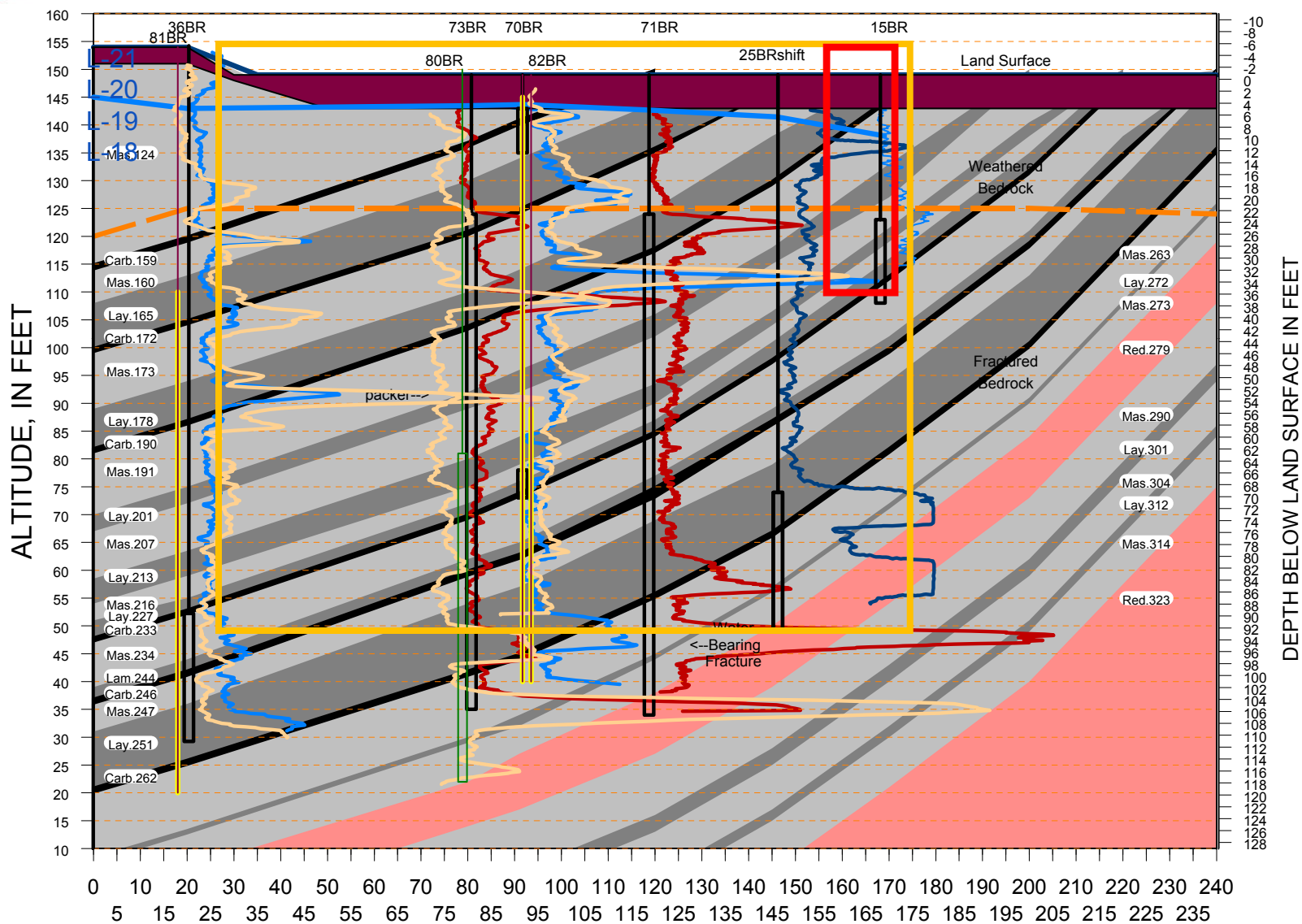
- Jet engine testing facility, 1950's to 1990's, West Trenton, NJ
- Decommissioned in 1998
- Pump & treat since mid-1990's
- 2001: NAWC chosen as fractured rock hydrology research site under USGS Toxics Substances Hydrology Program.
- TCE > 20 mg/L

From USGS



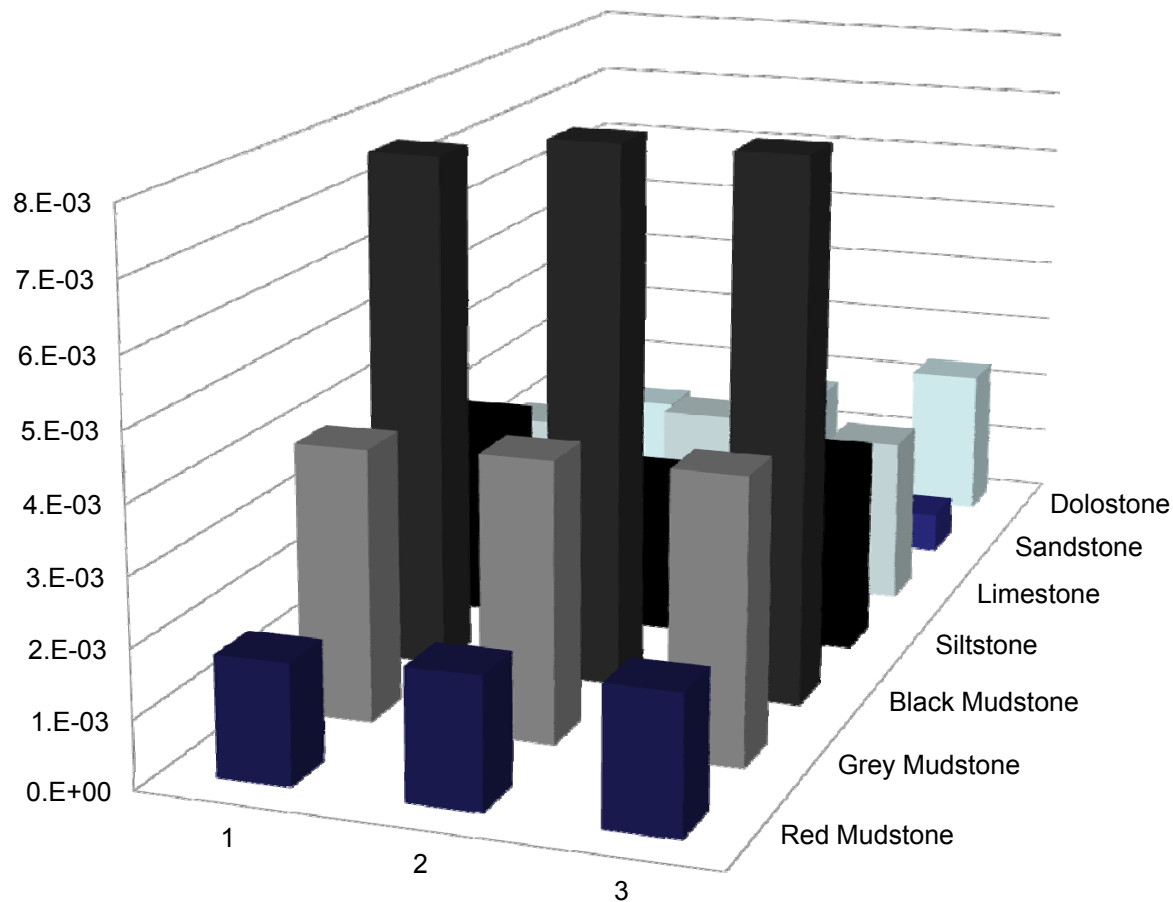


TCH Pilot
Test Location



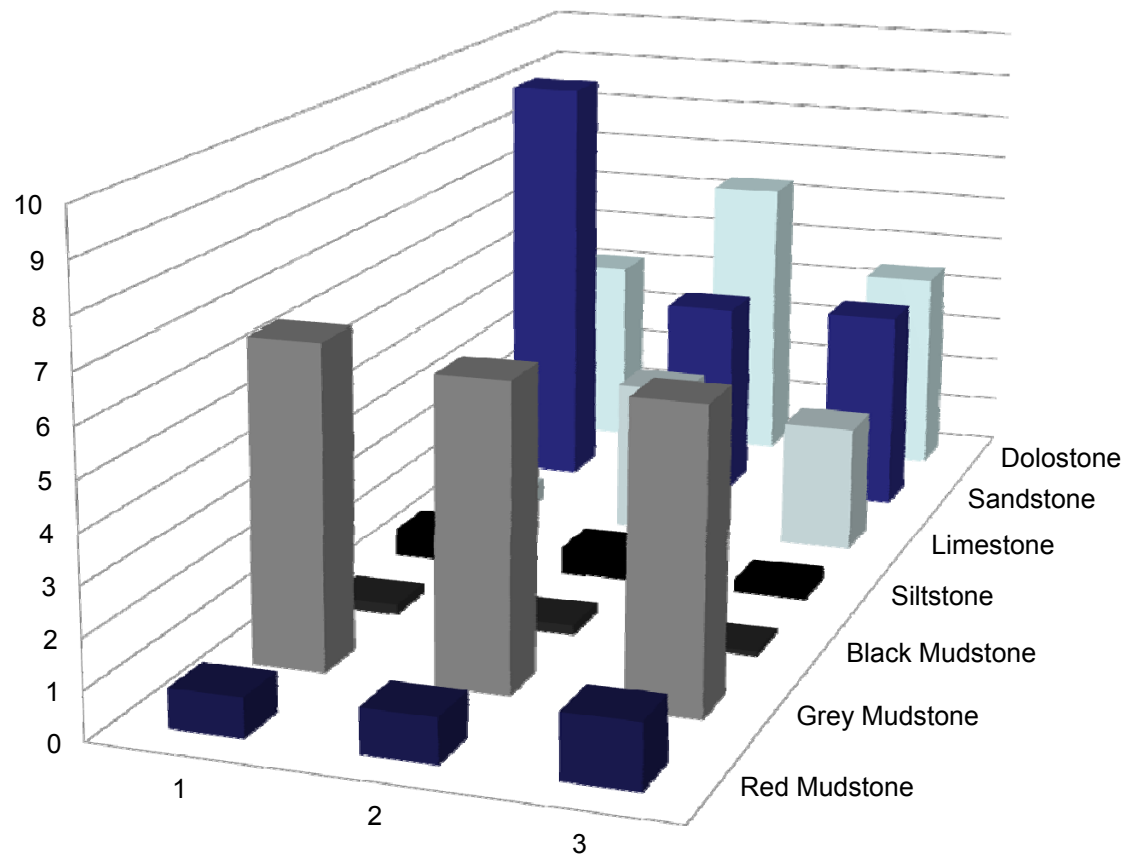
Performance Assessment: Physical Properties

Fraction organic carbon (F_{oc})



Performance Assessment: Physical Properties

Matrix Porosity (%)

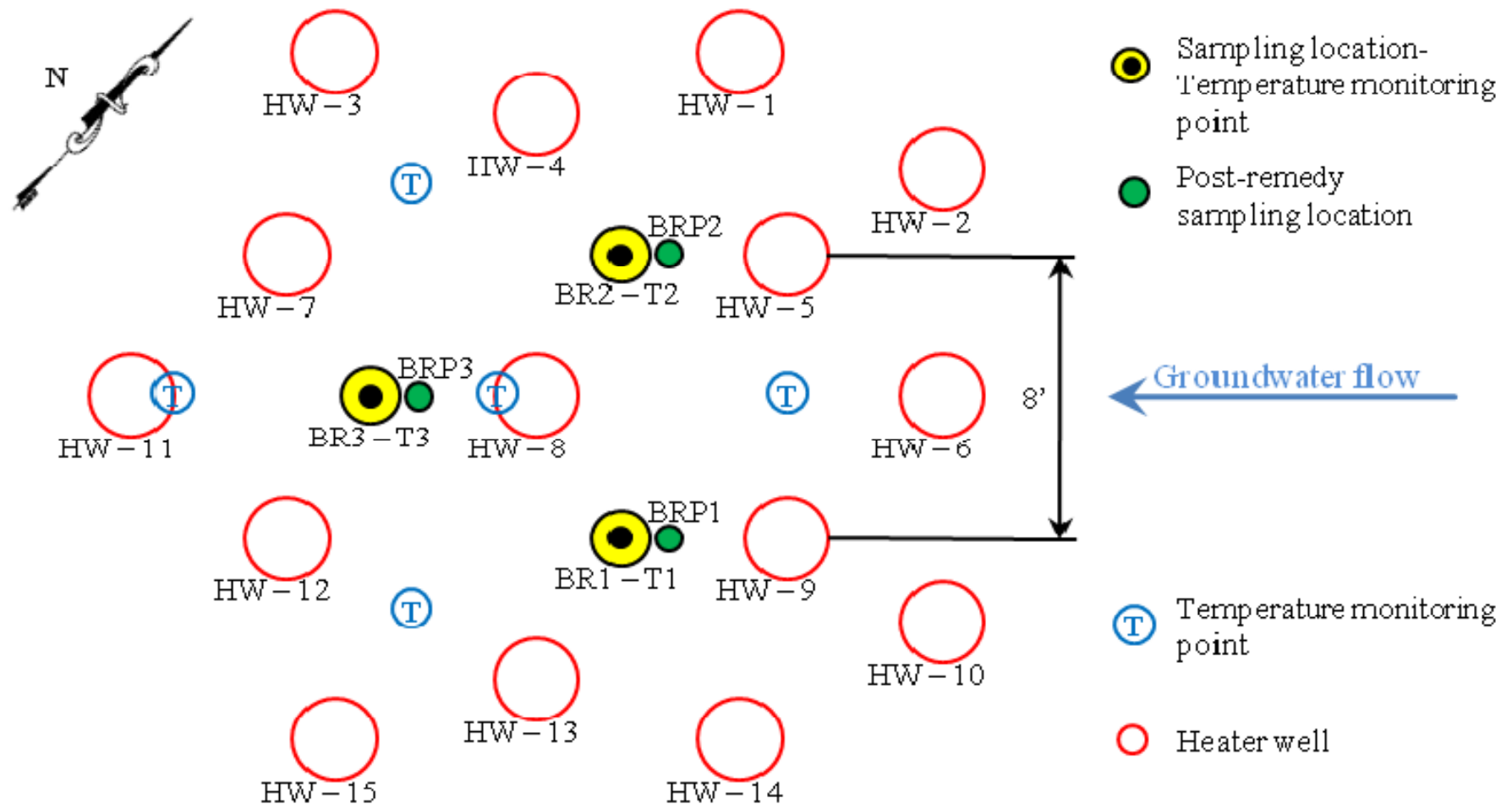


Performance Assessment: Field Demo

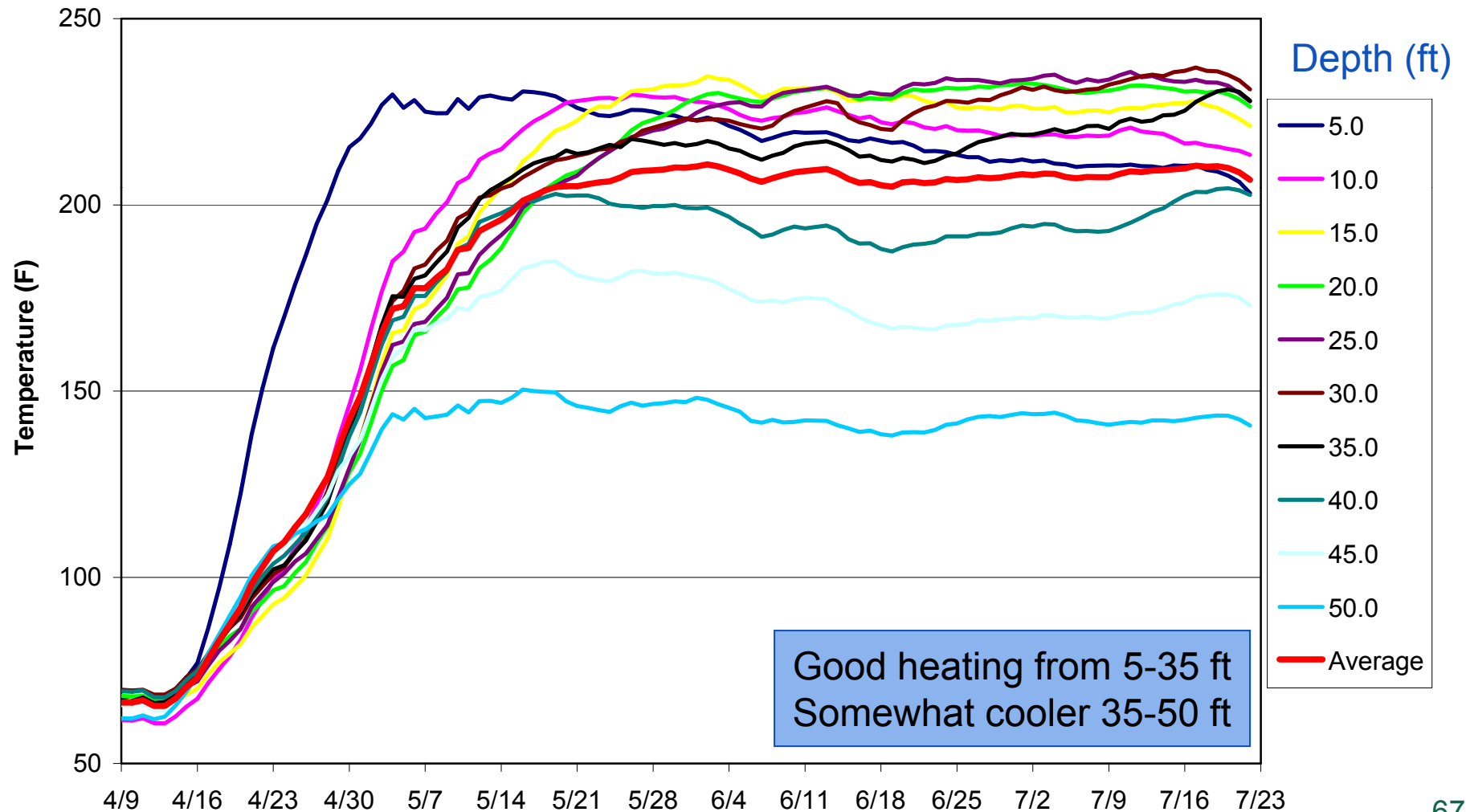




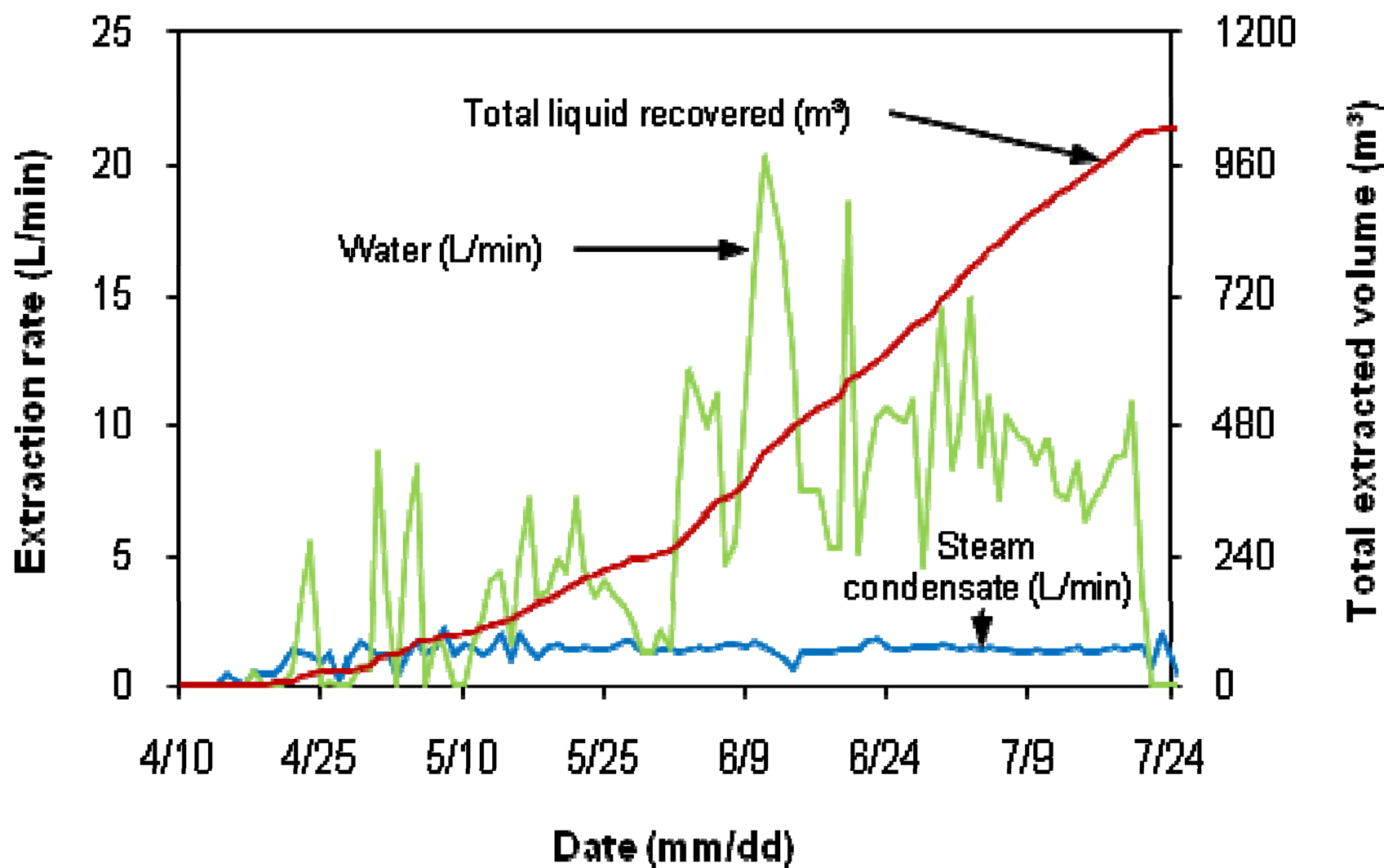
Well Configuration



Field Demo Rock Temperatures – Averages per depth

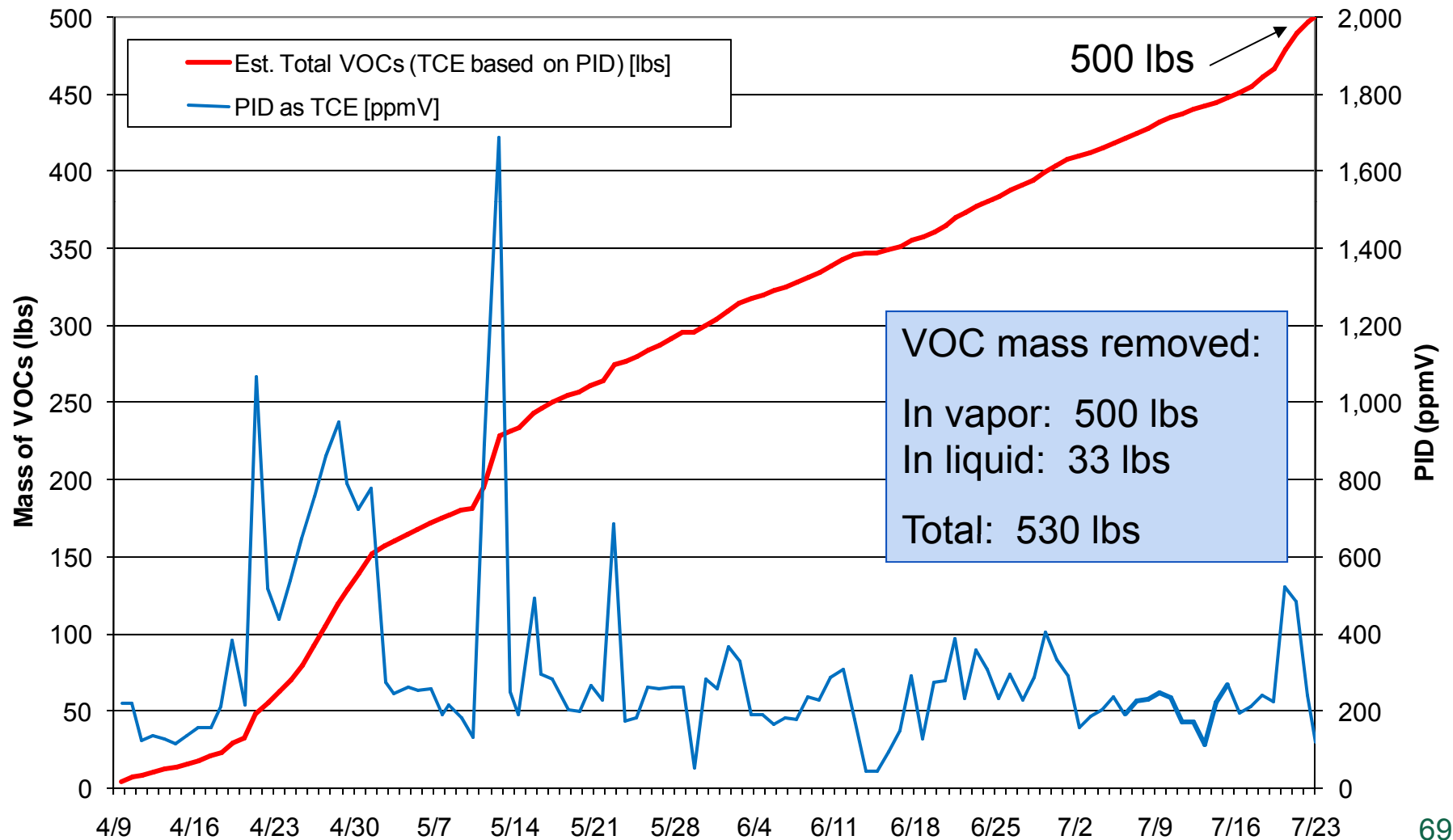


Fluids Extracted



Performance Assessment

Field Demo VOC mass removal





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ESTCP

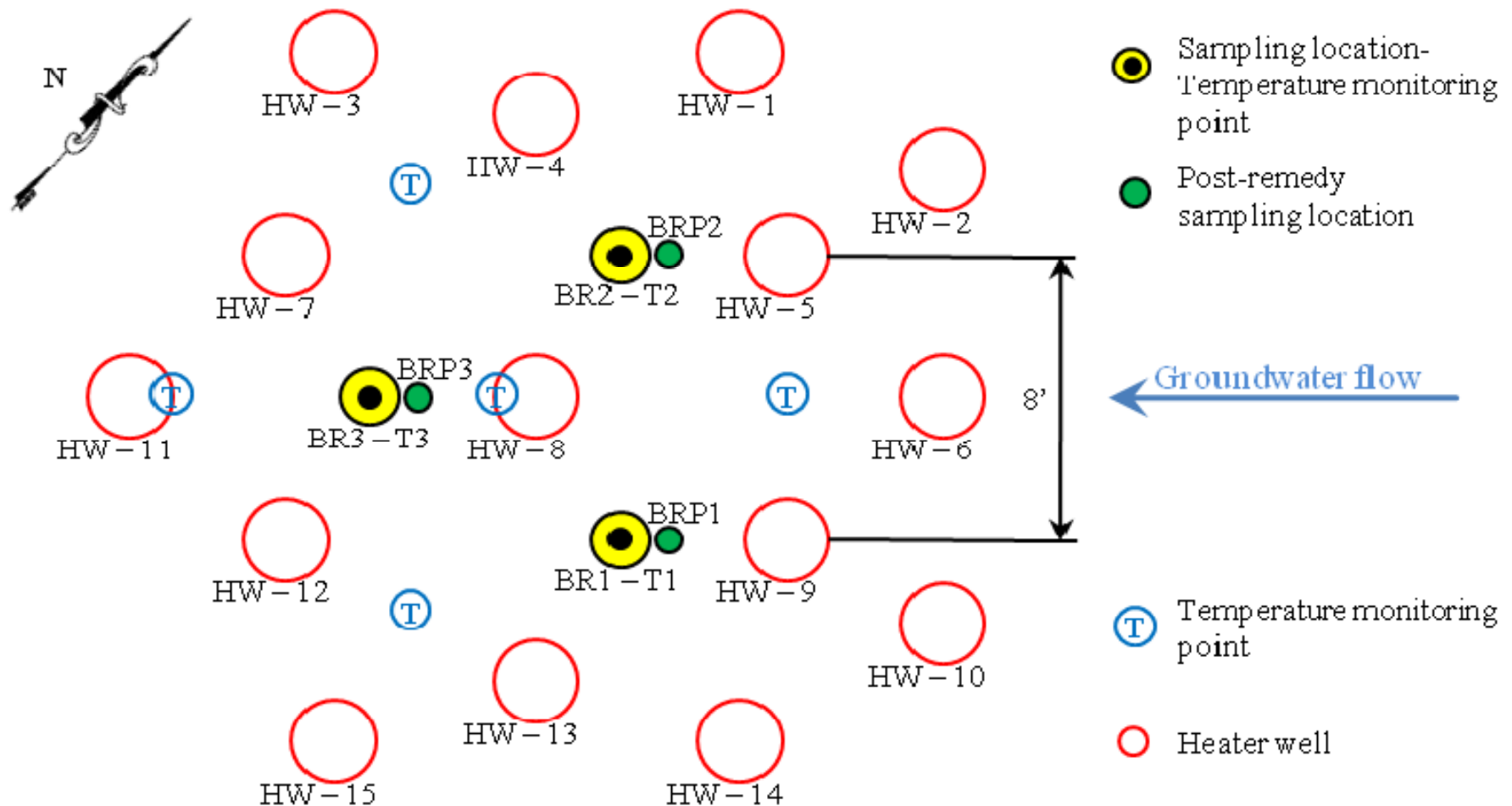
Performance Assessment

Collection & Analysis of Rock Samples for Treatment Confirmation





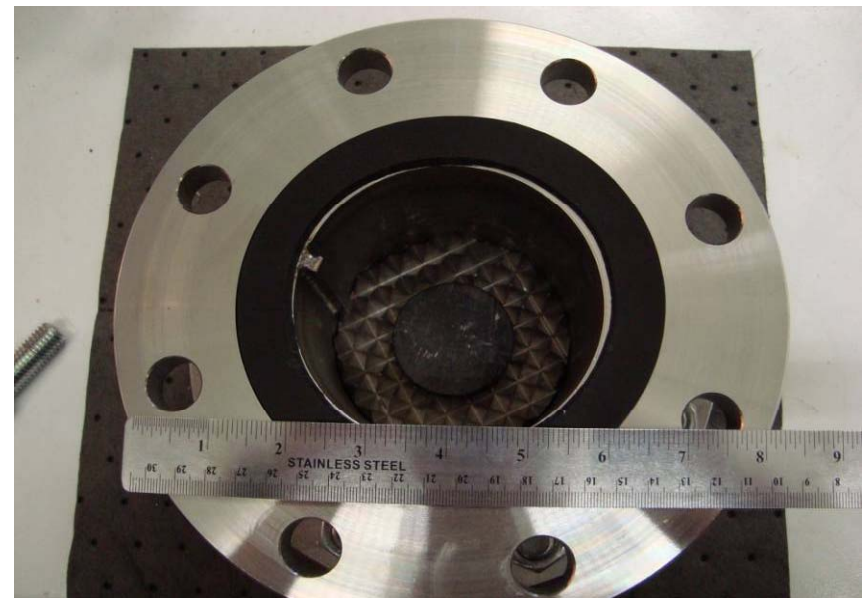
Performance Assessment: Field Demo





Performance Assessment

Collection & Analysis of Rock Samples for Treatment Confirmation



***Rock crusher
(Queen's University)***



Performance Assessment Summary

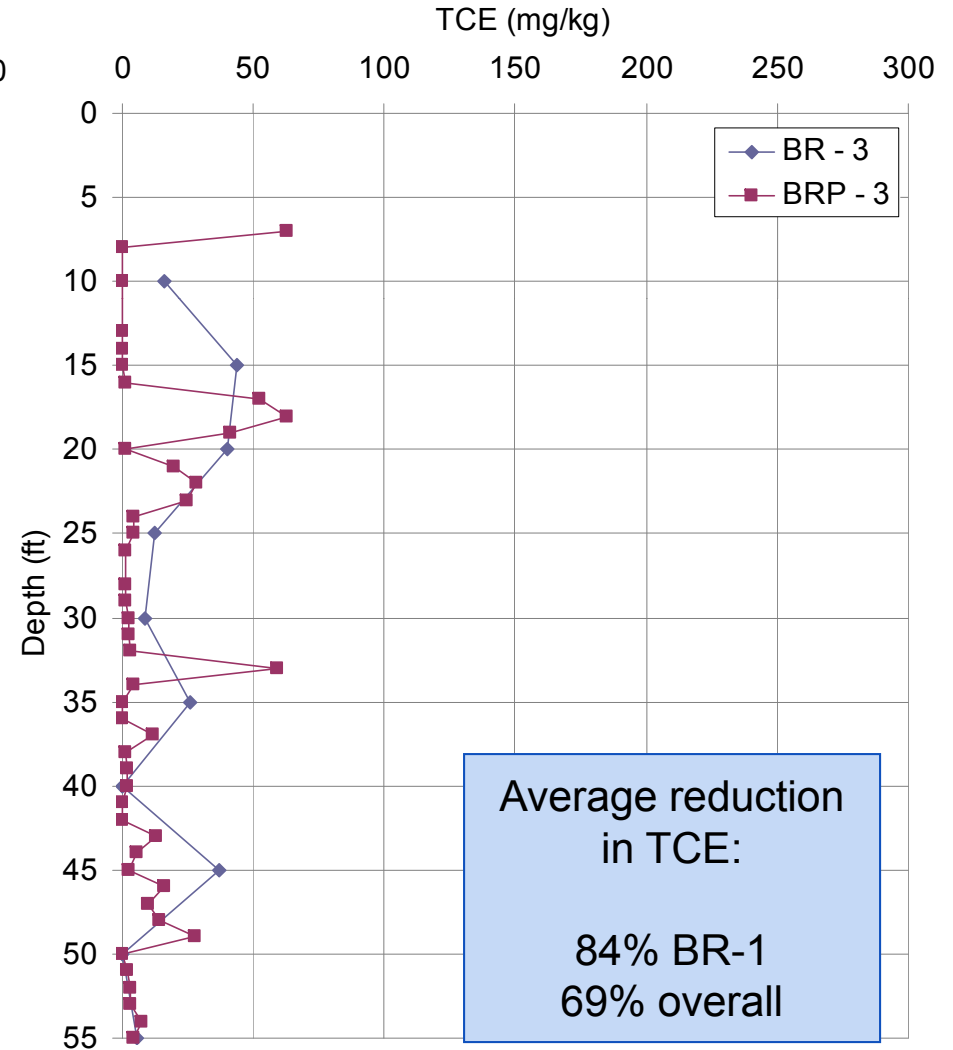
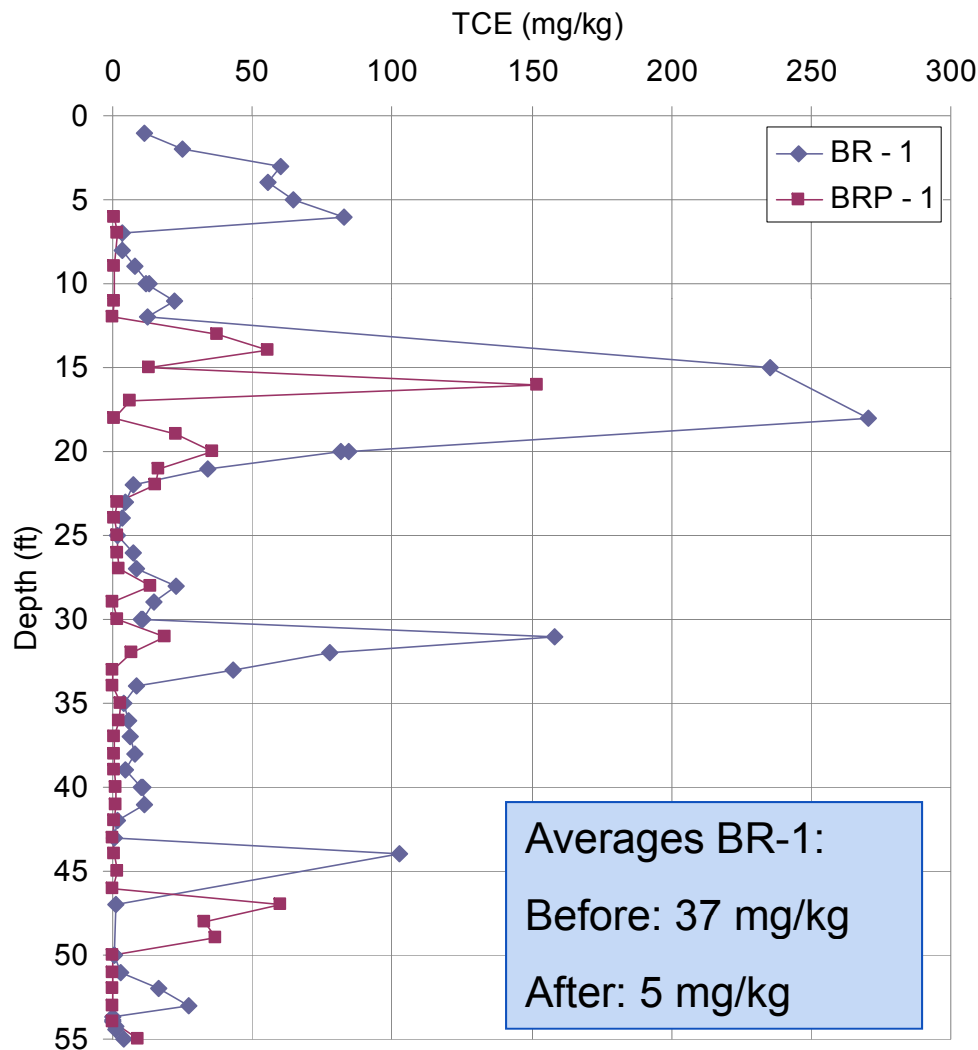
Collection & Analysis of Rock Samples for Treatment Confirmation



Crushed samples

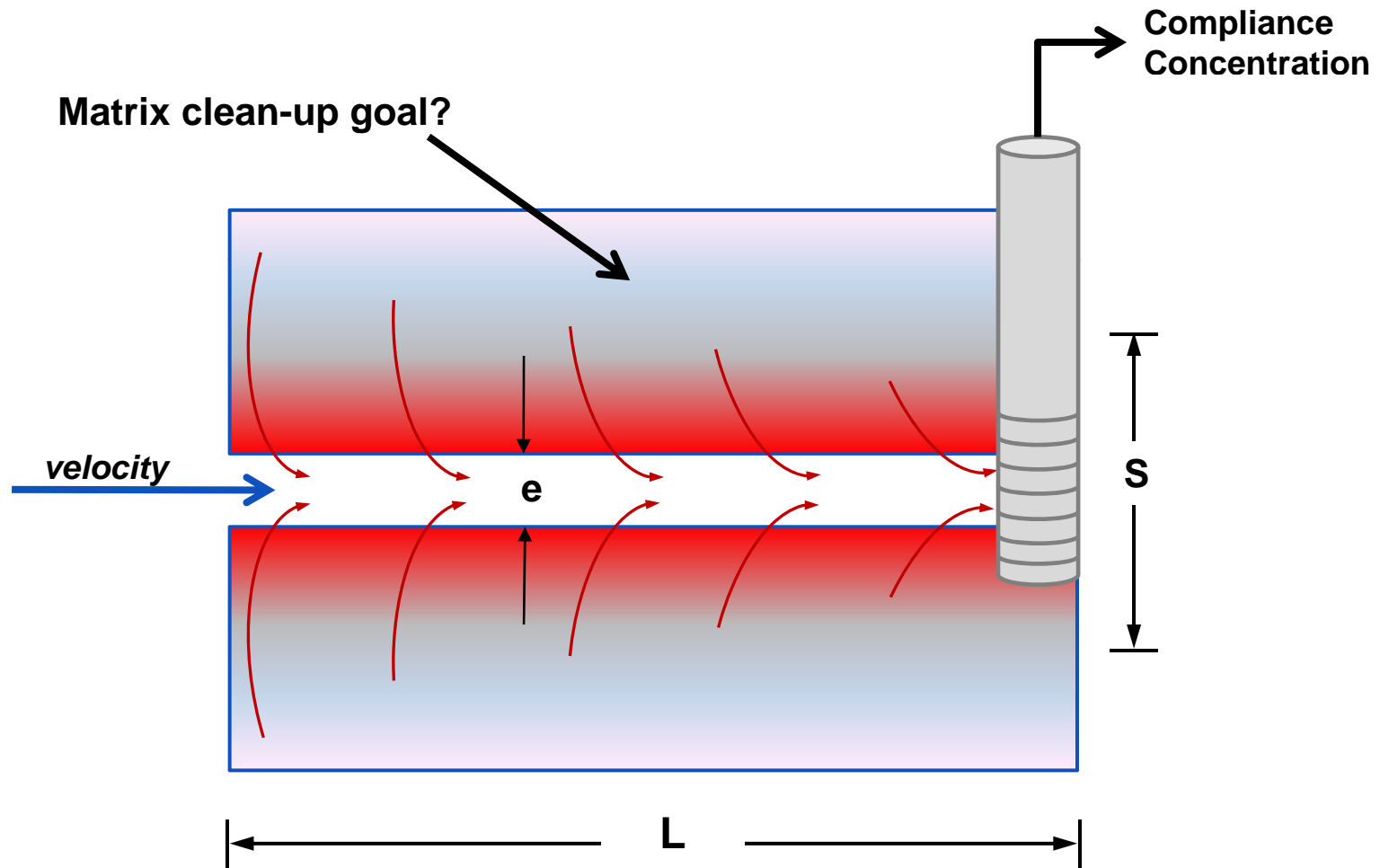
Performance Assessment

TCE Concentration in Rock Samples



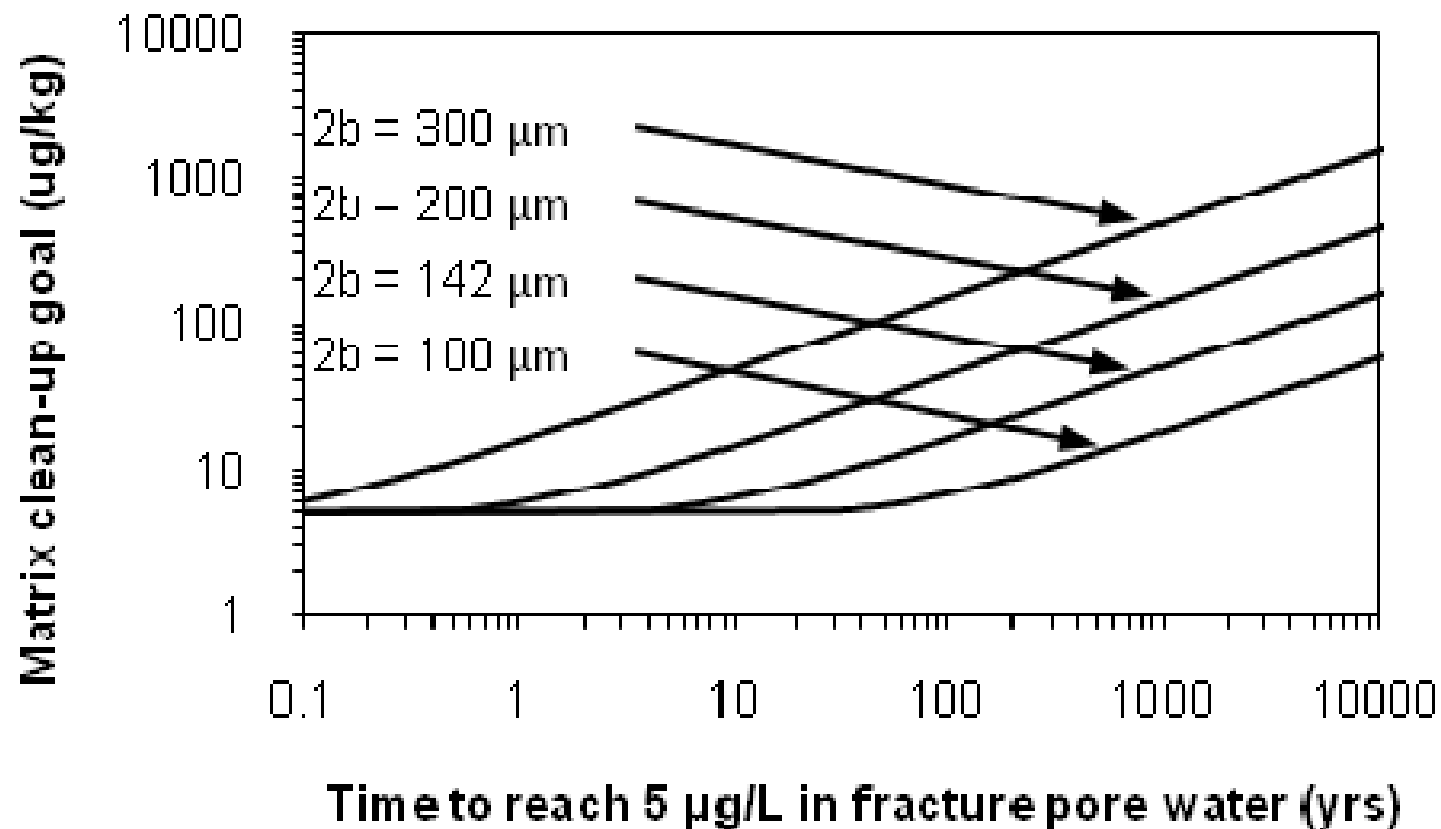


Rock Matrix Clean-up Goals



Example Output

($z = 100$ m, $S = 5$ m, $e = 142$ μm , matrix porosity = 3.3%, matrix $f_{oc} = 0.008$)



TOPIC #4 – Field parameters to measure



TOPIC #4 – Field parameters to measure in evaluating use of a thermal remedy in bedrock

- Bulk hydraulic conductivity (hydraulic testing)
- Hydraulic gradient
- Fracture spacing (aperture can be calculated)
- Matrix porosity, permeability, and fraction organic carbon
- VOC concentrations in matrix
- Thermal properties of rock matrix

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Simulating Thermal Treatment of Fractured Rocks

Ron Falta
Clemson University
faltar@clemson.edu



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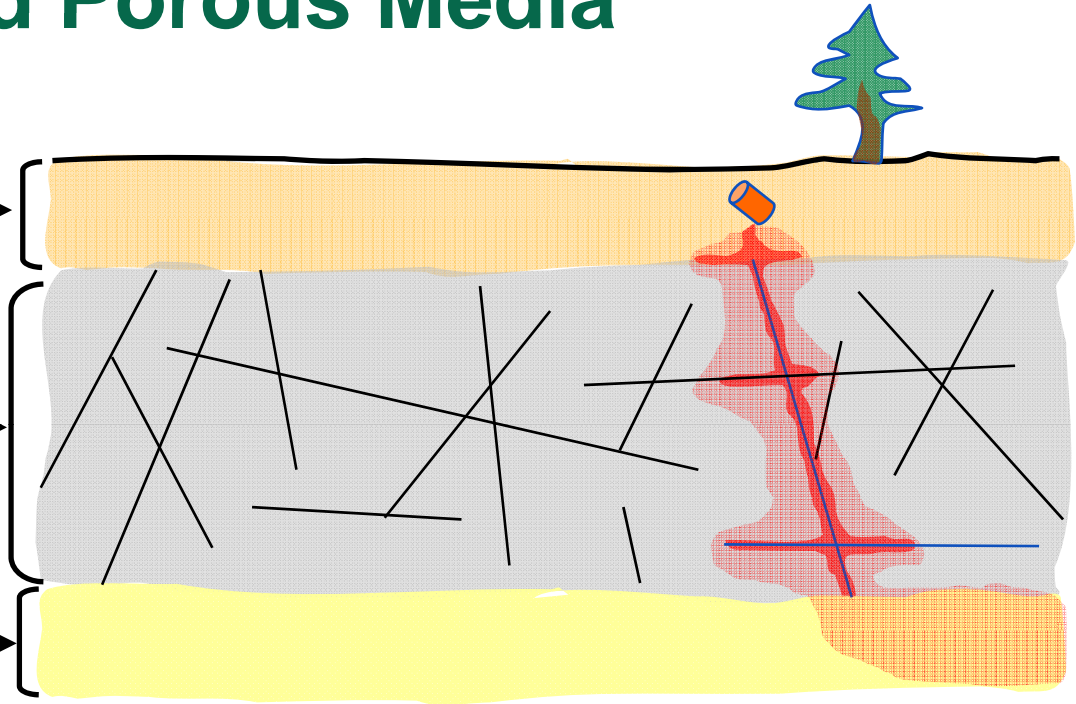


Fractured Porous Media

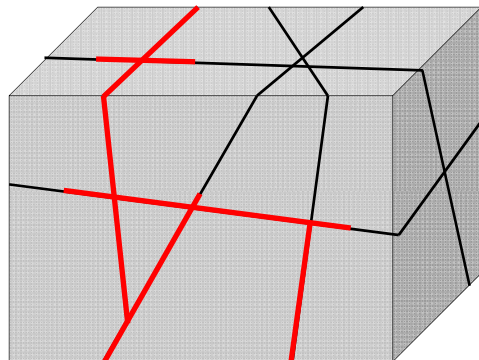
Unfractured soil layer

Fractured rock
(limestone, sandstone,
basalt, volcanic tuff) or
unconsolidated material
(clay, silt)

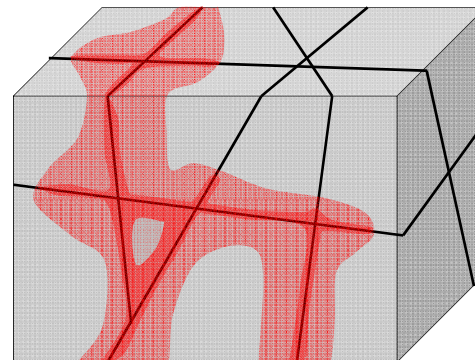
Unfractured rock or
sediment layer



Shortly after a DNAPL spill



Later time – mostly dissolved





OUTLINE

- Key Processes
 - ◆ Energy balance and cost to heat to boiling temperature
 - ◆ Energy required to boil off water
 - ◆ Steam stripping of dissolved chlorinated solvents
- Numerical Multiphase Flow Models
 - ◆ Existing models and capabilities
 - ◆ Simulation of Clemson laboratory experiments
- Field Scale Simulations
 - ◆ Challenges and approaches
 - ◆ Multiple Interacting Continua (MINC)
 - ◆ Simulation examples



Energy Balance: heating up to boiling temperature

$$\Delta M^h = (1 - \phi) \rho_R C_R \Delta T + \phi S_w \rho_w C_w \Delta T$$

ϕ = porosity (.01-.4)

ρ_R = rock grain density 2300-2700 kg/m³

ρ_w = liquid water density 1000 kg/m³

C_R = rock grain heat capacity 800-1200 J/kg°C

C_w = liquid water heat capacity 4200 J/kg°C

S_w = water saturation (0-1)



Example: cost to heat 1 cubic meter

$$\Delta M^h = (1 - \phi) \rho_R C_R \Delta T + \phi S_w \rho_w C_w \Delta T$$

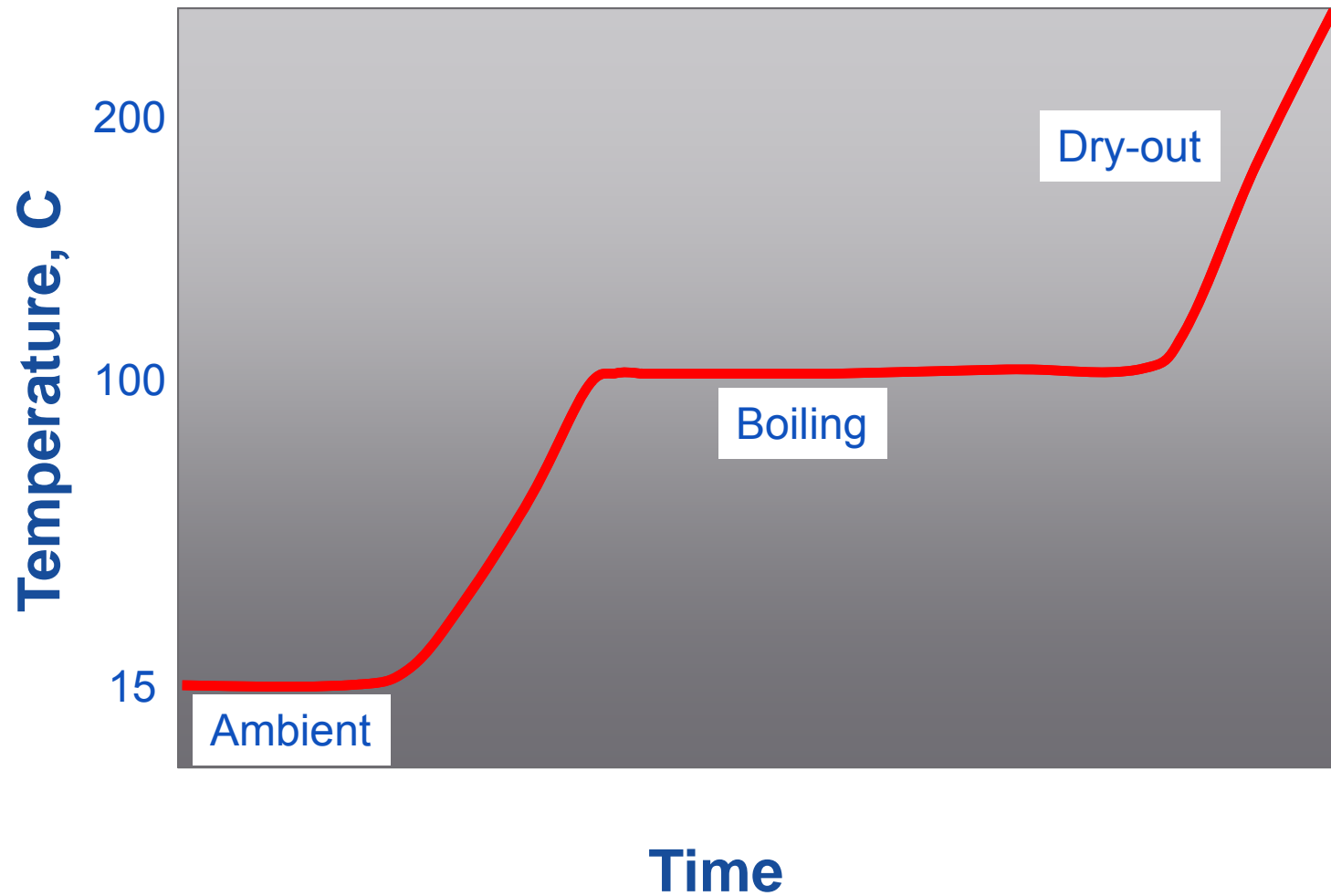
$$= (1 - .2)(2650)(1000)(90) + (.2)(1)(1000)(4200)(90)$$

$$= 191 \text{ MJ/m}^3 + 76 \text{ MJ/m}^3 = 267 \text{ MJ/m}^3$$

One kW-hr = 3.6 MJ, so 74 kW-hr to heat 1 m³

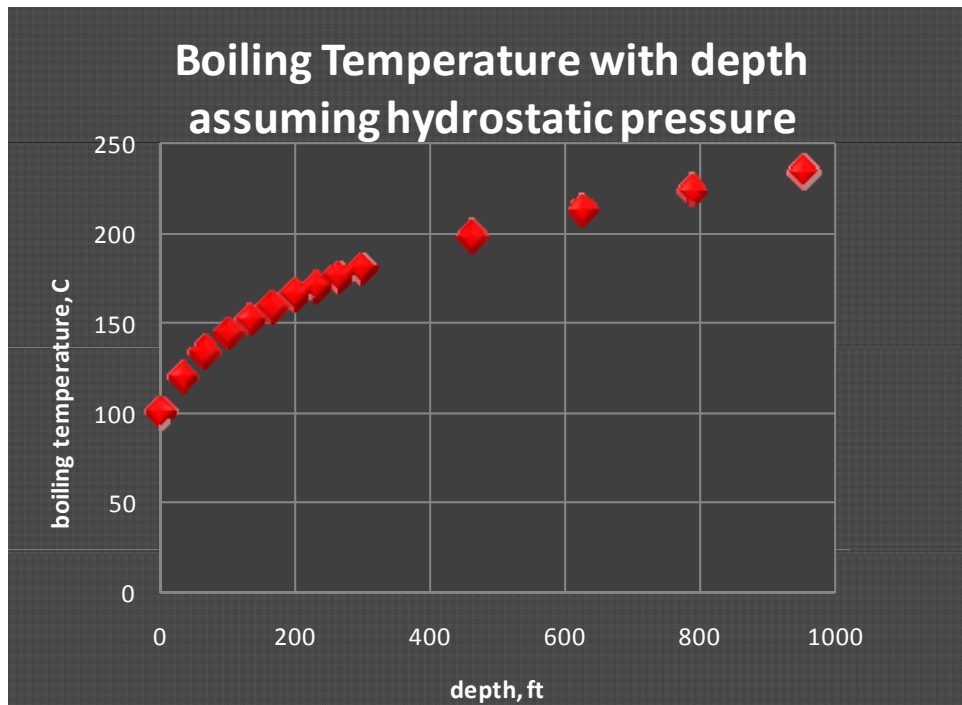
At \$0.10/kW-hr, this would cost \$7.40/m³

Typical heating pattern with time





Boiling temperature depends on pressure (and dissolved components)



- Under vacuum conditions, the boiling point is lower:
0.7 atm – boiling at 90 C
0.5 atm – boiling at 80 C

Dissolved volatile compounds and gases also depress the boiling temperature

Steam stripping of dissolved volatiles: Udell's 1996 analysis

Assume equilibrium batch conditions in some control volume. Steam vapor is generated by boiling, and leaves the volume, carrying contaminant vapors

$$\frac{1}{\rho_w} \frac{d(M_w^{H_2O} C_w^c)}{dt} = \frac{1}{\rho_g} \frac{dM_w^{H_2O}}{dt} C_g^c$$

rate of change of
dissolved contaminant
mass = rate of volumetric
steam generation x gas concentration

$M_w^{H_2O}$ = mass of liquid water

C_w^c = dissolved concentration

C_g^c = gas concentration



After some calculus and algebra...

$$\frac{C_w^c}{C_{w,0}^c} = \left(\frac{M_w^{H_2O}}{M_{w,0}^{H_2O}} \right)^{\left(\frac{H \rho_w}{\rho_g} - 1 \right)}$$

$H = \text{Henry's const.}$

The exponent is huge because liquid water is ~ 1600 times denser than steam vapor. Typical values for H at steam temperatures are about 0.3 to 7 depending on the chemical



Steam Stripping

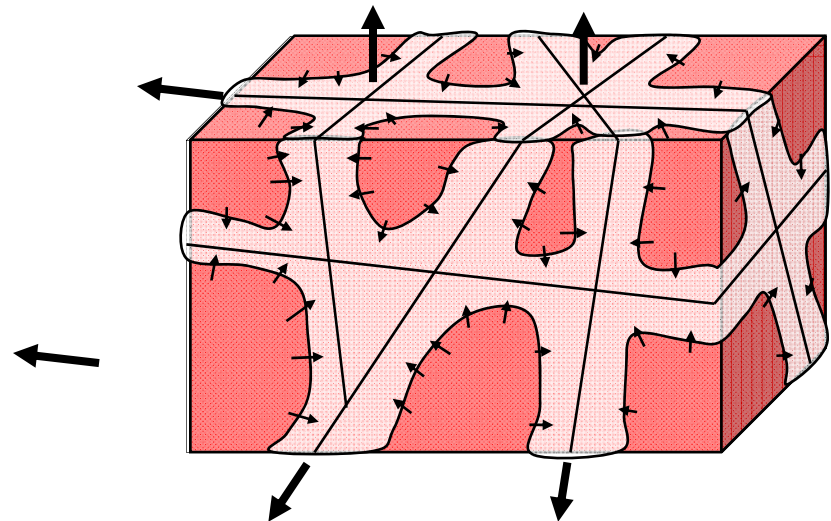
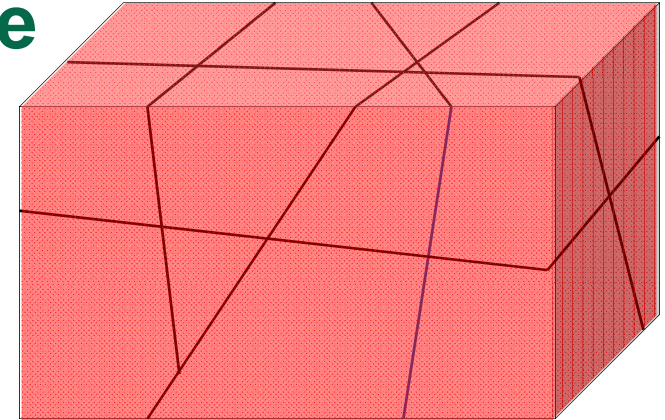
- Steam stripping results in geometric reductions in dissolved concentrations of volatiles
- The stripping effect only occurs as liquid water is converted to vapor, and leaves the system
- **A system may be at the boiling temperature, with highly variable rates of water phase change – this has tremendous impact on contaminant removal!**



Once the rock is hot, boiling starts. Details of the boiling are very important

- Contaminant removal only occurs in the locations where liquid water is being converted to vapor
- The boiling may be well distributed in the rock, or it may be localized around the fractures

Entire rock mass heated to steam temperature

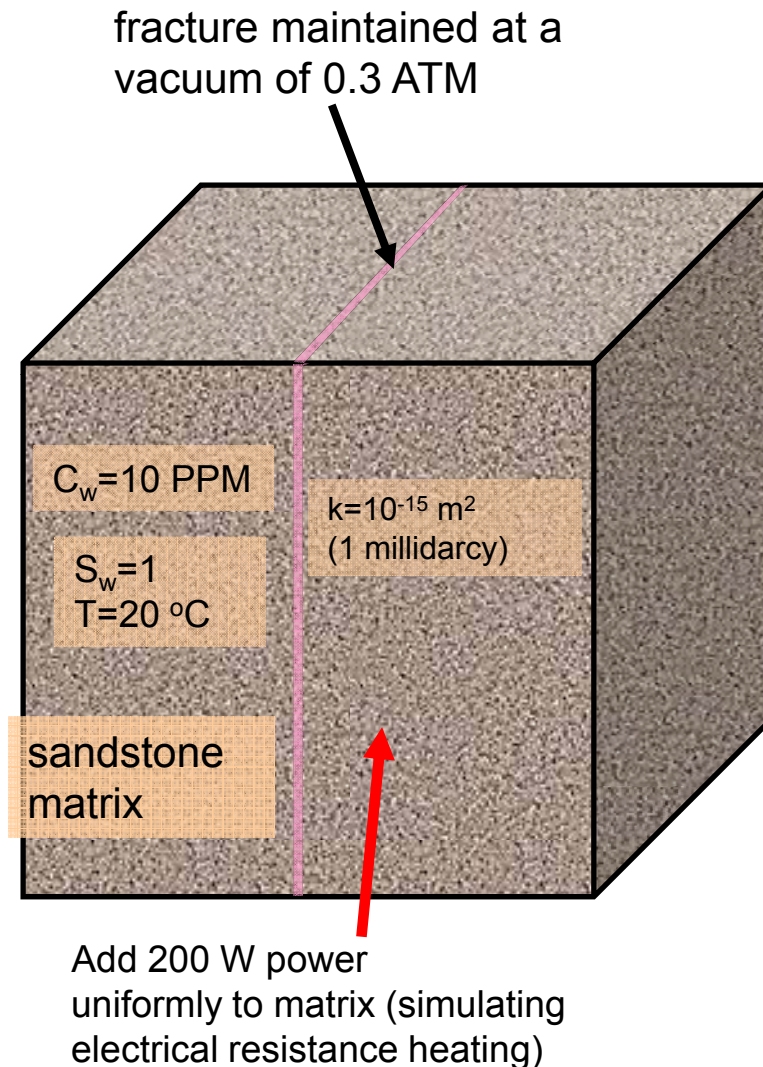


1D Simulations (T2VOC)

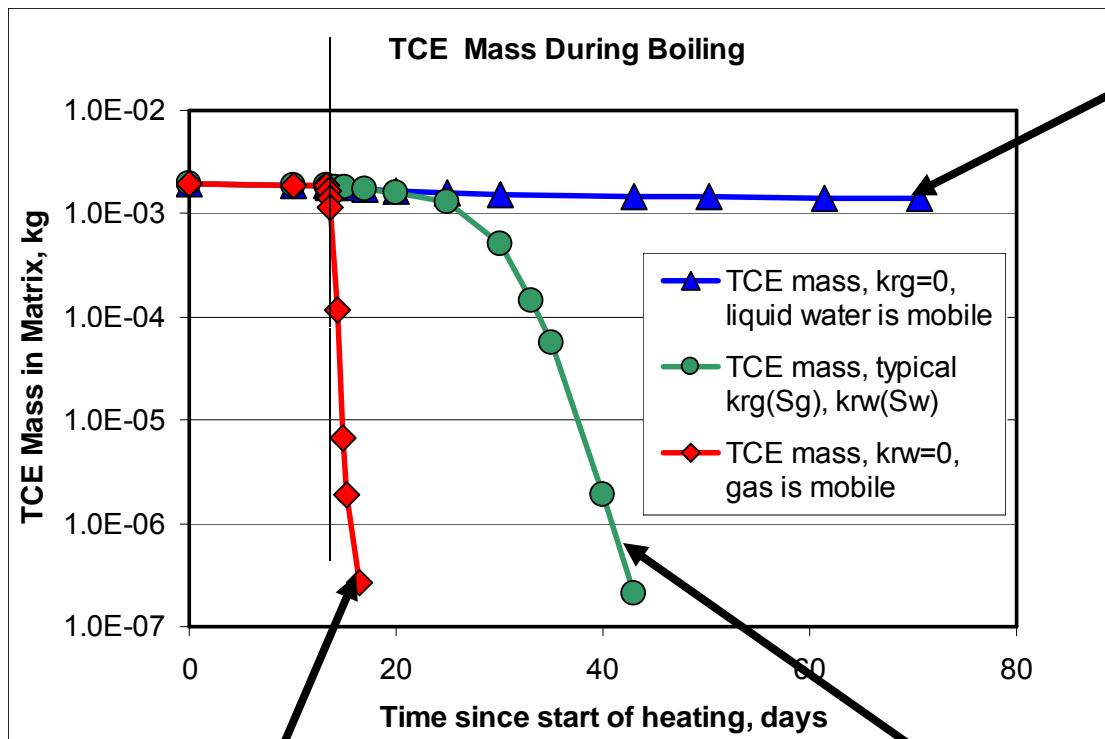
- 1 m³ block of rock with a single fracture. Fracture and matrix initially saturated with water containing 10 ppm TCE.
- Heat the block with 200 W power.
- Drop pressure in fracture and simulate mass in matrix with time

Consider three conditions:

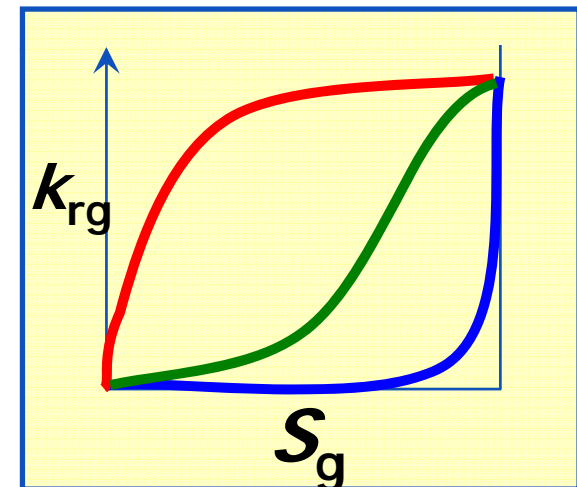
- a.) steam is mobile in matrix
- b.) steam is immobile in matrix
- c.) intermediate vapor mobility



RESULTS: 1-D Simulations



Vapor phase forms as isolated bubbles in matrix, pushing liquid water into fracture where it boils. Heat to sustain fracture boiling comes from thermal conduction.



Vapor forms in matrix and is mobile, flowing freely to fracture. All boiling occurs in matrix, and steam stripping effect is similar to Udell (1996) model

Initially vapor phase pushes liquid water into fracture where it boils. Later, vapor phase becomes more mobile and flows out to fracture. Boiling moves from fracture to matrix with time



Energy required to boil away pore water

- The heat of vaporization of water is about 2,260,000 J/kg
- From the previous heating example, there was about 192 kg of liquid water in each cubic meter of rock
- to boil away 50% of this water would require 217 MJ, or about 60 kW-hr. At \$0.10/kw-hr, this would cost \$6.00/m³ which is comparable to the cost to raise the temperature up to the normal boiling point
- Our laboratory experiments and numerical simulations show excellent contaminant removal with 40-60% liquid water removal during heating.



Numerical Models for Steam Remediation

- There are many existing multiphase flow codes that can be used for modeling thermal remediation in fractured heterogeneous porous media. A partial list:
 - ◆ T2VOC (Falta et al., 1992; Falta et al., 1995)
 - ◆ NUFT (Nitao, 1993)
 - ◆ COMFLOW (Forsyth, 1994)
 - ◆ MUFTE (Helmig et al., 1994)
 - ◆ MAGNAS (Panday et al., 1995)
 - ◆ STOMP (White and Oostrom, 1996)
 - ◆ TMVOC (Pruess and Battistelli, 2002)

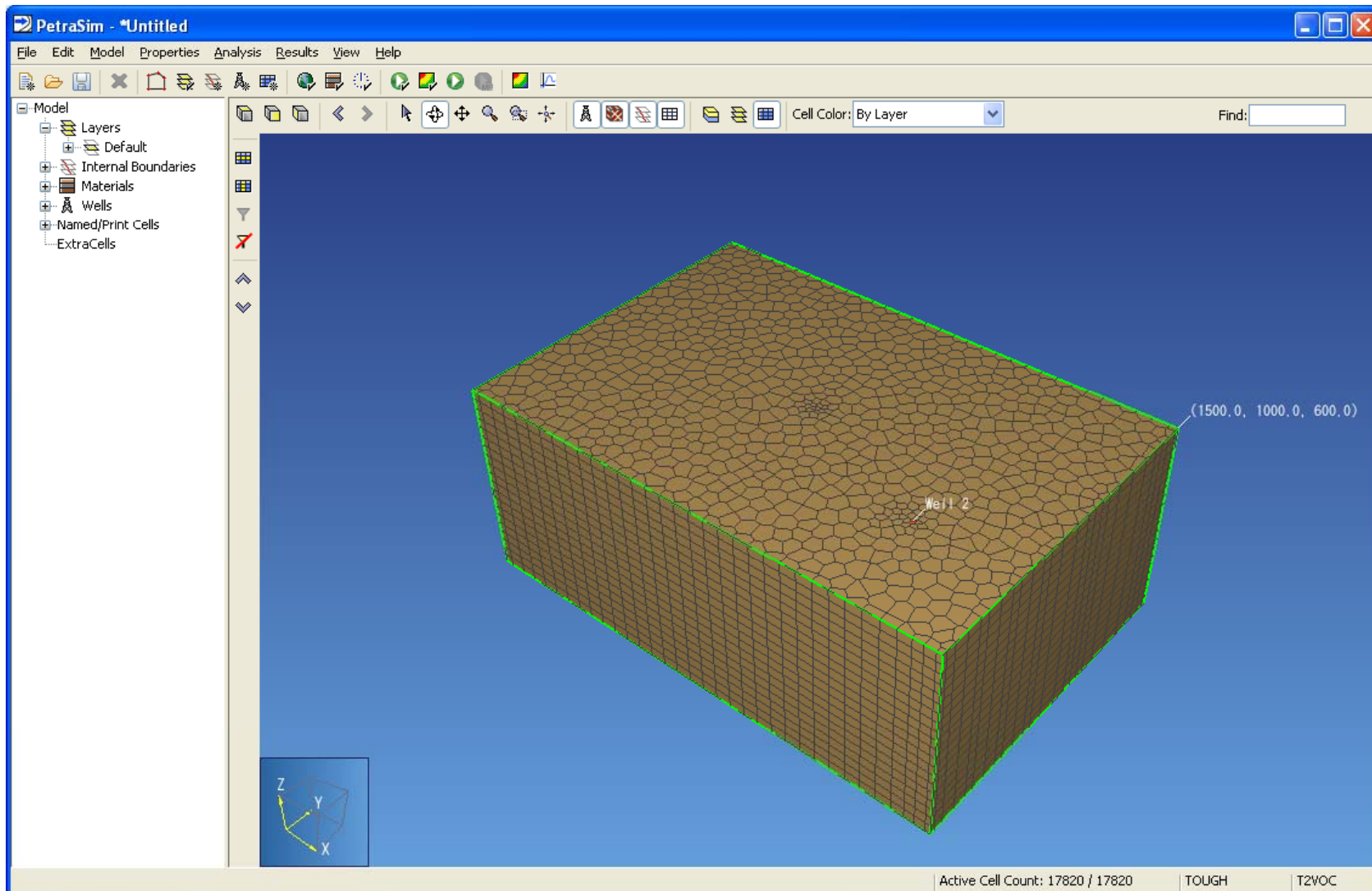
These codes have similar numerical formulations and process capability



TMVOC (Pruess and Battistelli, 2002)

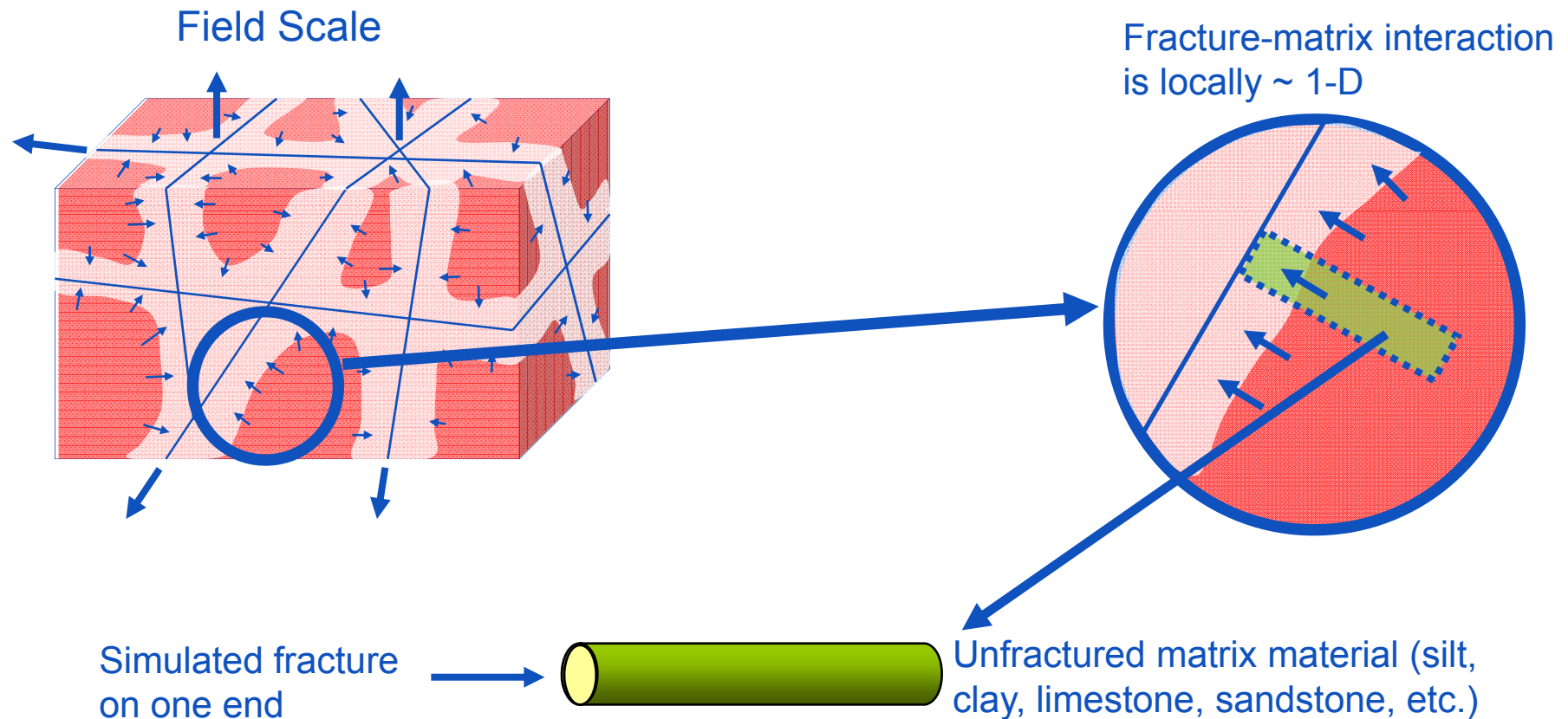
- 3D integral finite difference formulation for fractured and heterogeneous media
- 3 phase flow (gas, aqueous, NAPL)
- Full heat transfer and thermodynamics with evaporation, boiling and condensation of water and multicomponent NAPLs
- Temperature dependent vapor pressure, solubility, and Henry's constants for contaminants
- Multiphase diffusion with tortuosity effects
- Assumes local (gridblock) chemical equilibrium with linear adsorption isotherms, first order decay of dissolved contaminants
- Includes noncondensable gases (air, etc), and can simulate dry superheated conditions
- Maximum temperature is limited to critical point of water (374 °C)

A GUI for TMVOC is available (PetraSim)



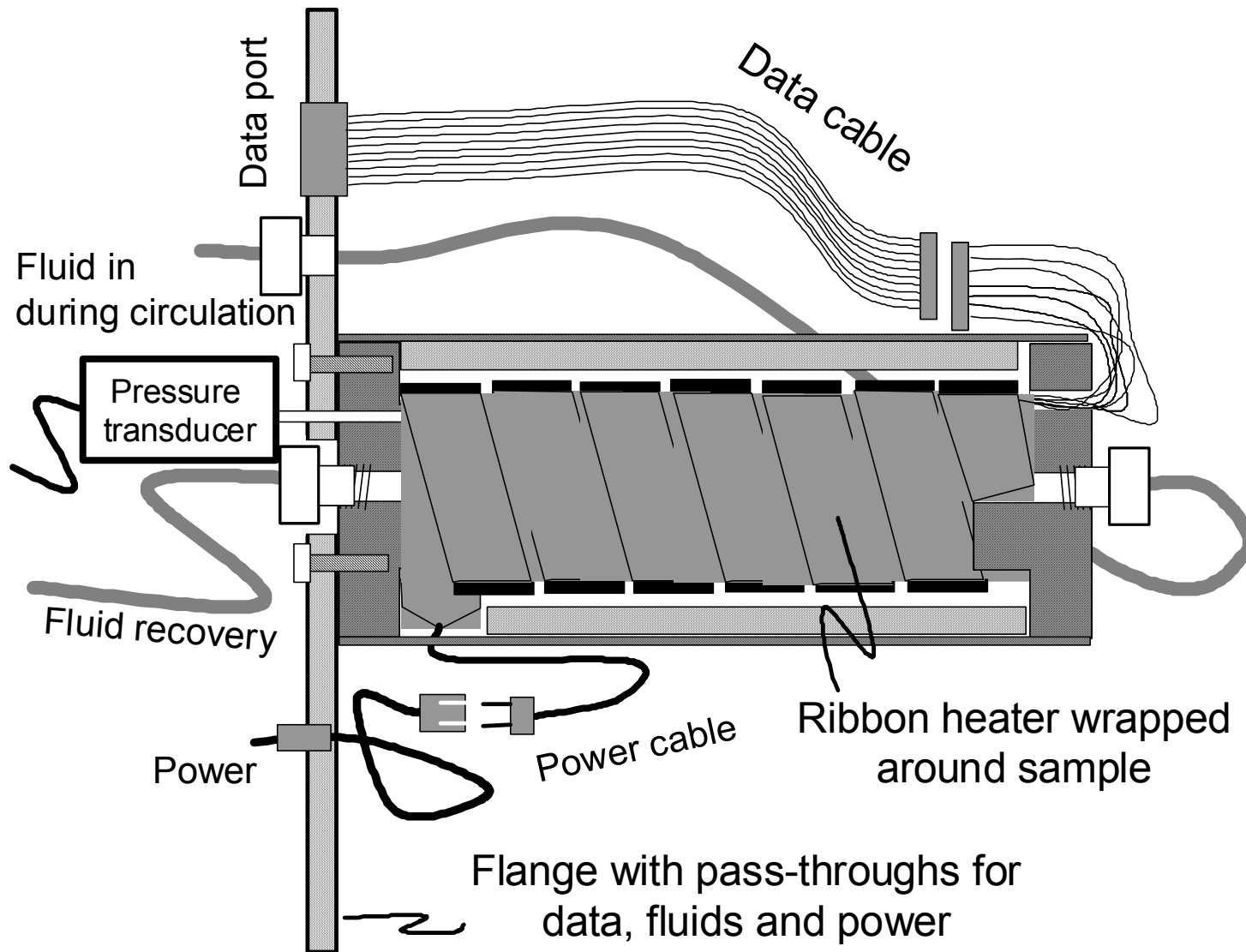


Simulation of Laboratory Experiments (SERDP ER-1553)



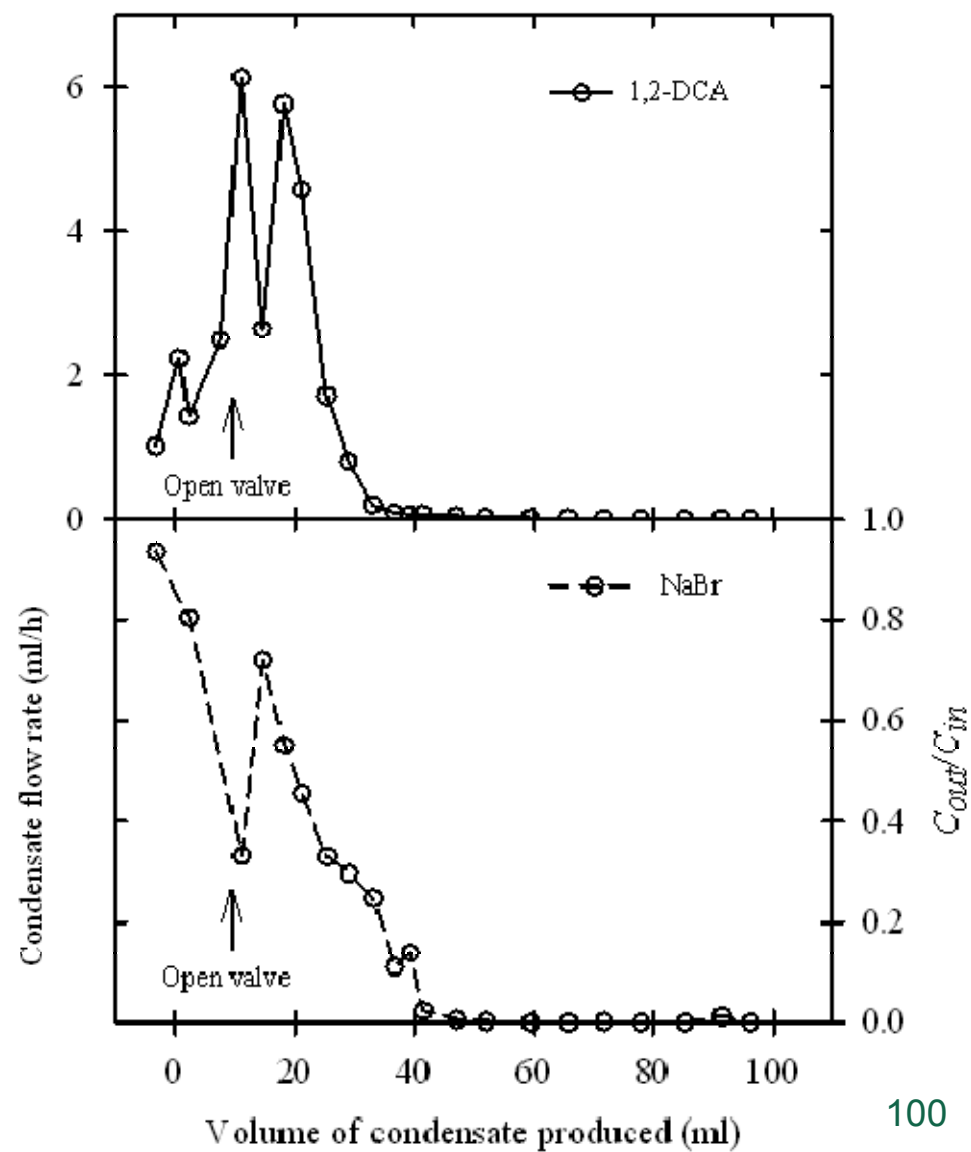
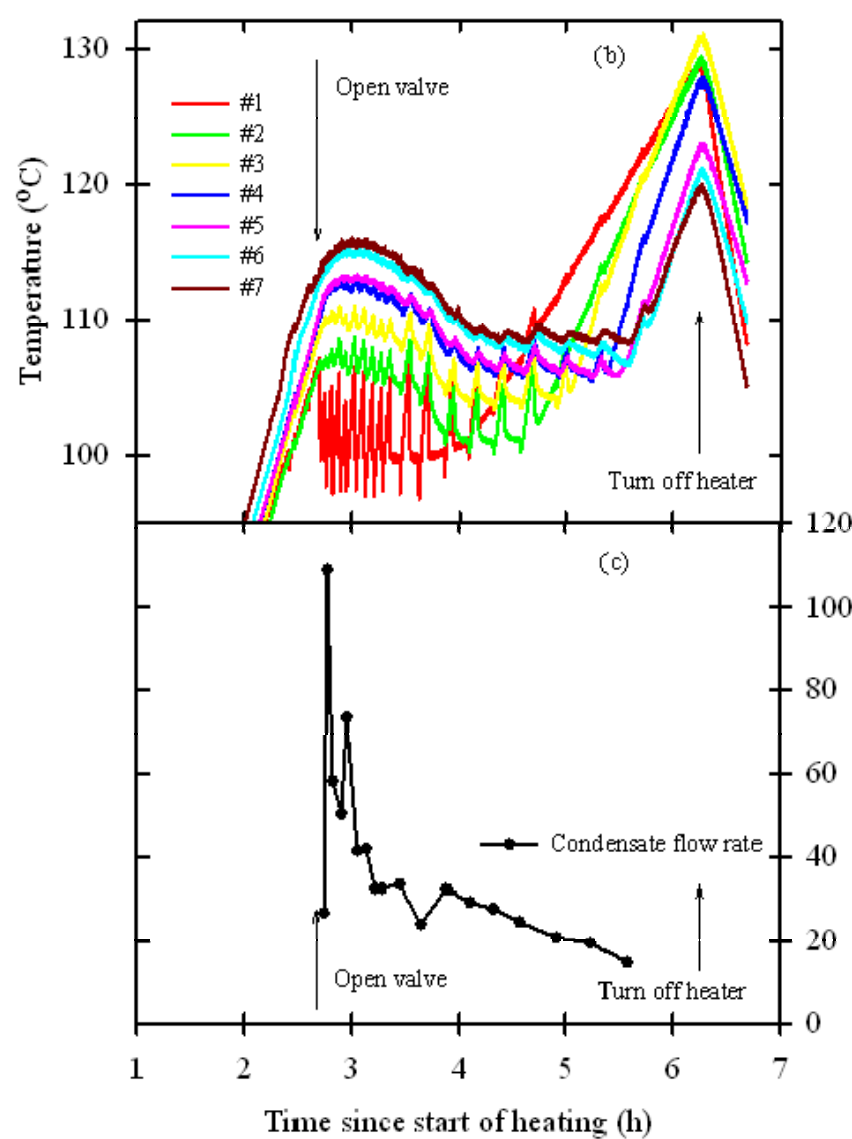


Experimental Setup



Experimental Results

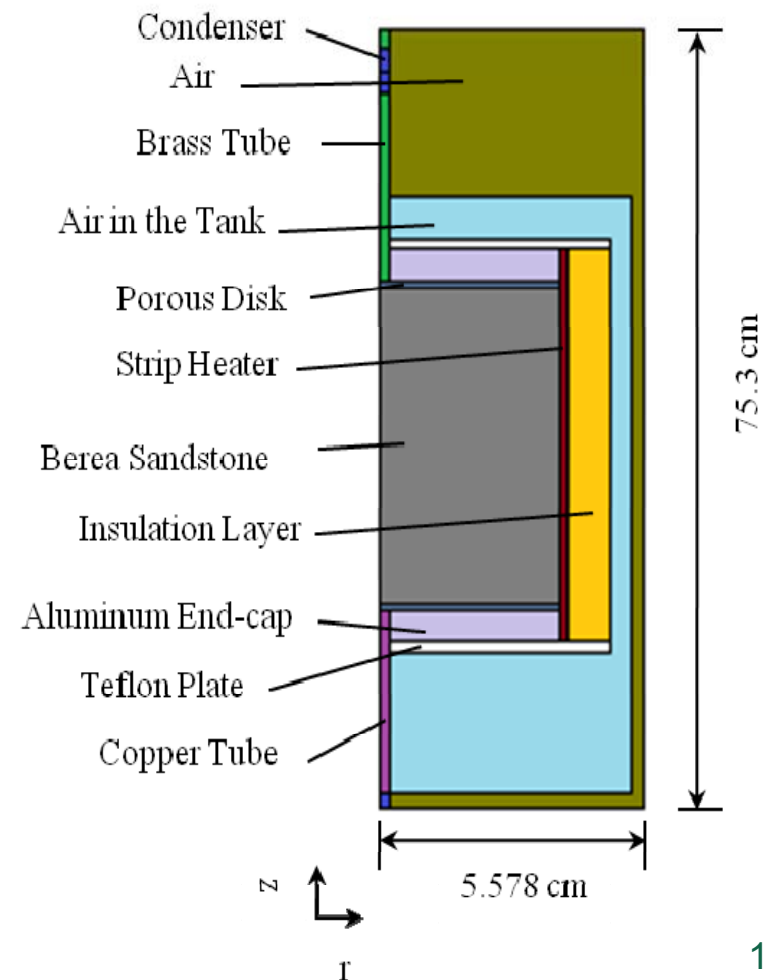
Chen et al., 2010



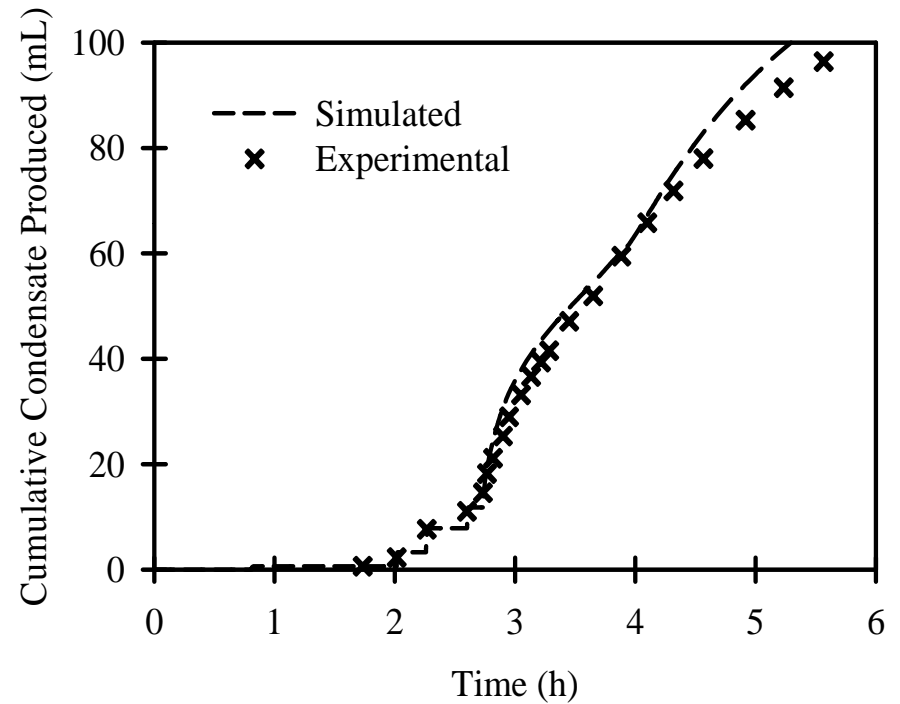
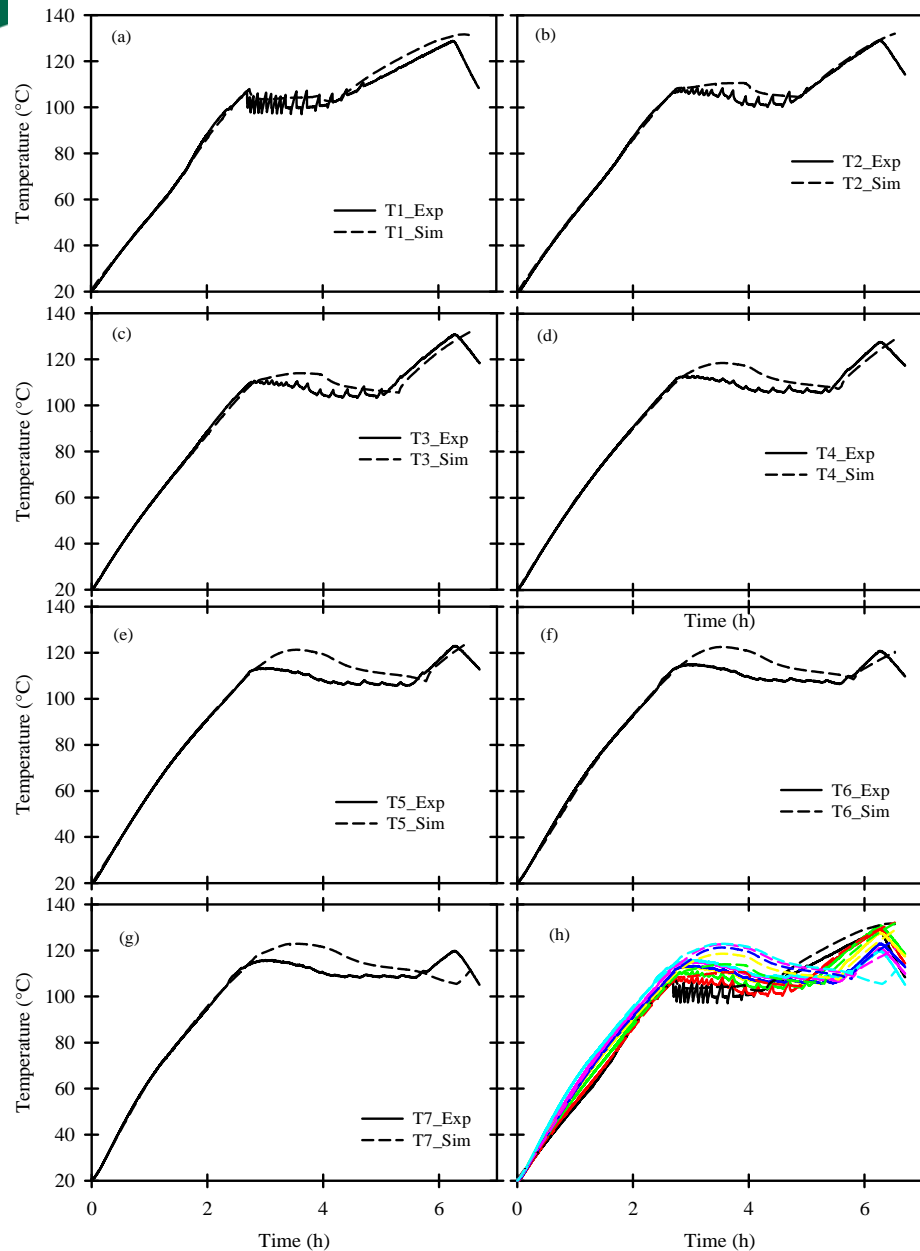


TMVOC model: 2d r-z model. Simulating end effects is critical here

Subdomain	Porosity	Permeability (m ²)	Density (kg/m ³)	Thermal conductivity (W/m°C)
Berea sandstone	0.167	1.5×10^{-13}	2491	3.57 (wet) 1.75 (dry)
Heater	0.001	1.0×10^{-18}	501.2	1.07
Porous disk	0.16	1.0×10^{-10}	3950.0	41.22
Aluminum end-cap	0.001	1.0×10^{-18}	2702	237
Outlet tube	0.0559	1.46×10^{-10}	8730	60
Condenser	0.0559	1.46×10^{-10}	1.0×10^{10}	60
Inlet Tube	0.14	3.15×10^{-10}	8940	400
Teflon Plate	0.001	1.0×10^{-18}	2200	0.5
Insulation Layer	0.01	1.0×10^{-18}	100	0.28



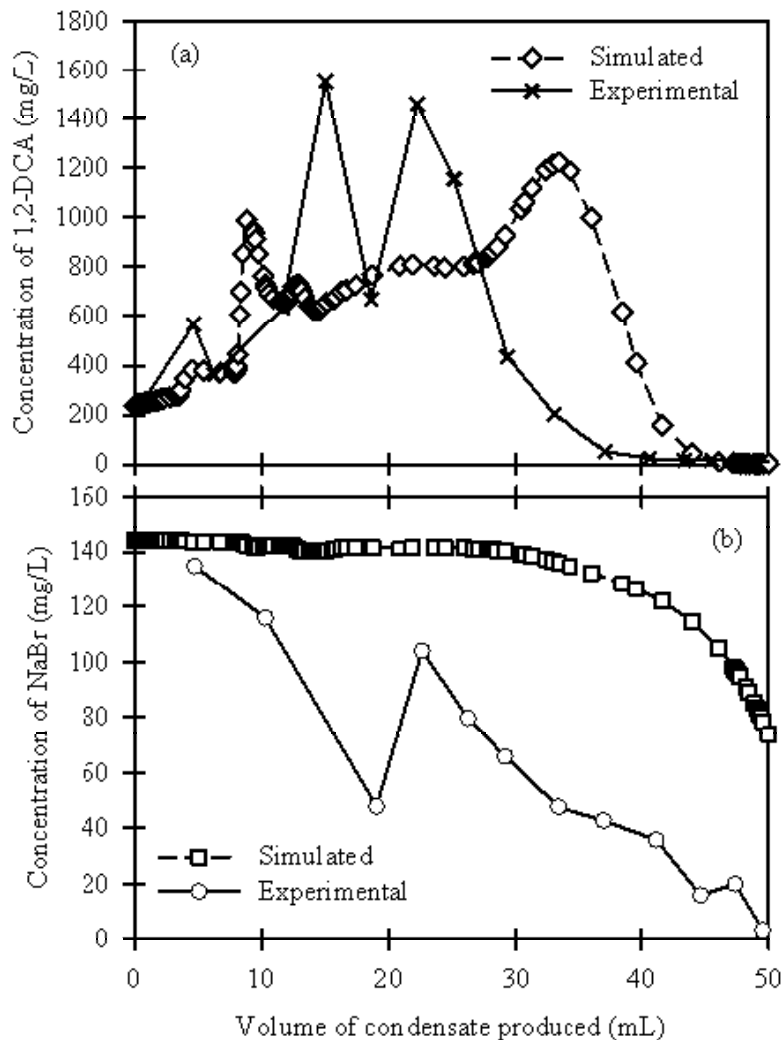
Simulation Results: temperature and condensate production



Chen et al., 2011

Simulation Results: temperature and condensate production

Chen et al., 2011



- Model is predicting a slower transition to vapor flow conditions
- Likely due to fact that we used measured air relative permeability; steam vapor relative permeability is probably higher
- Simulation and experiment both show complete DCA removal at 40% pore volume produced

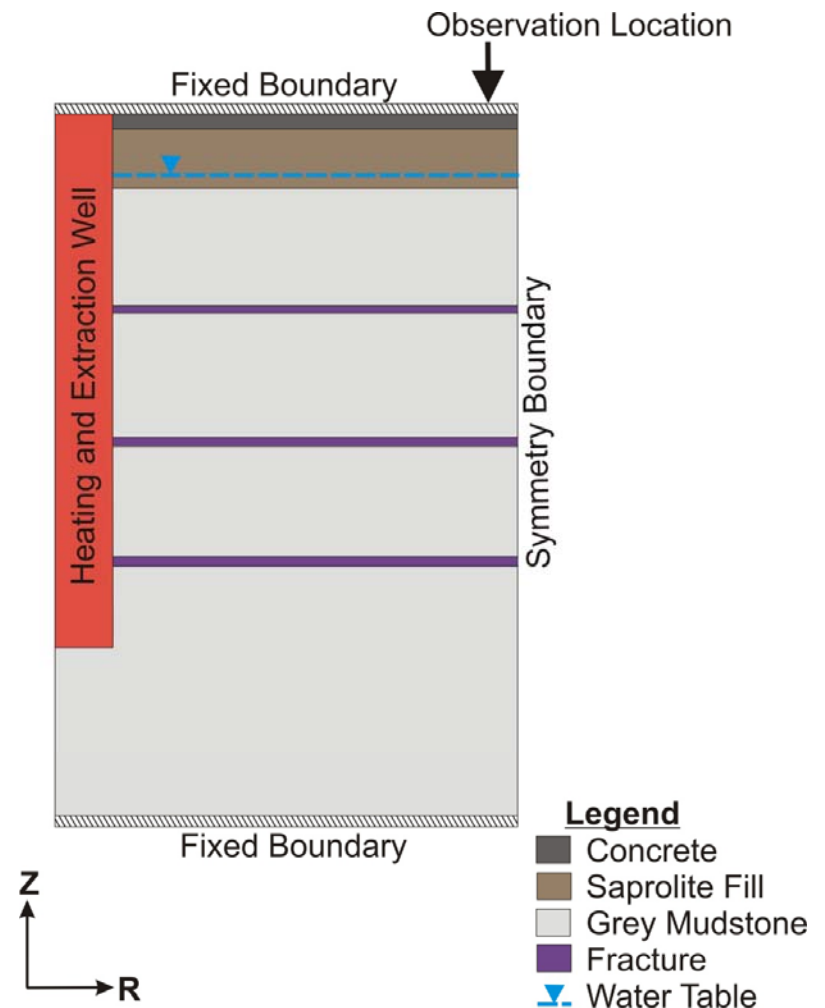


Field scale simulations of fractured systems

- Numerically challenging due to small size of fractures compared to large size of model
- Large contrasts in permeability and capillary pressure between fractures and rock matrix
- Discretization issues – need to discretize both the fractures (very small) and the matrix (very large), with transitions in size between the two
- Starting from liquid water conditions, gas phase evolution occurs in all boiling gridblocks – possibility of unstable phase transitions

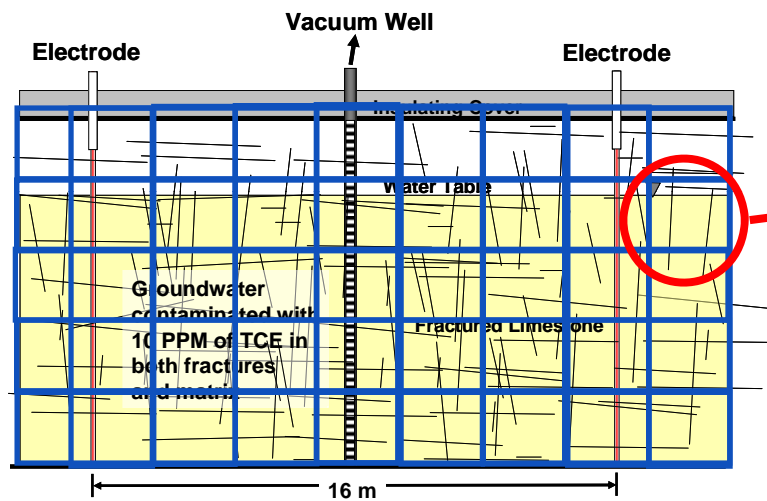
Discrete fracture model

- Normal discretization of fractures and matrix, small elements near fractures
- Most realistic model, but practically limited to simple fracture geometry
- Best for parallel sets of fractures due to computational limits



Wemp et al., 2011

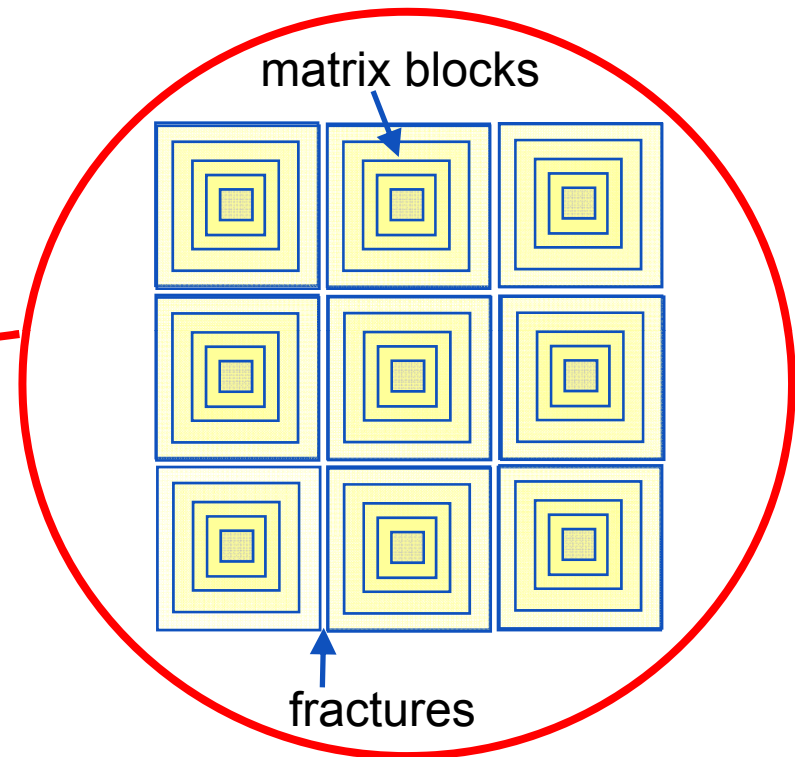
Multiple Interacting Continua (MINC) discretization



Spatial domain is discretized normally into volume elements

The fracture elements are globally connected in all directions.

This is similar to a dual porosity formulation, but gradients in the matrix are resolved much more accurately



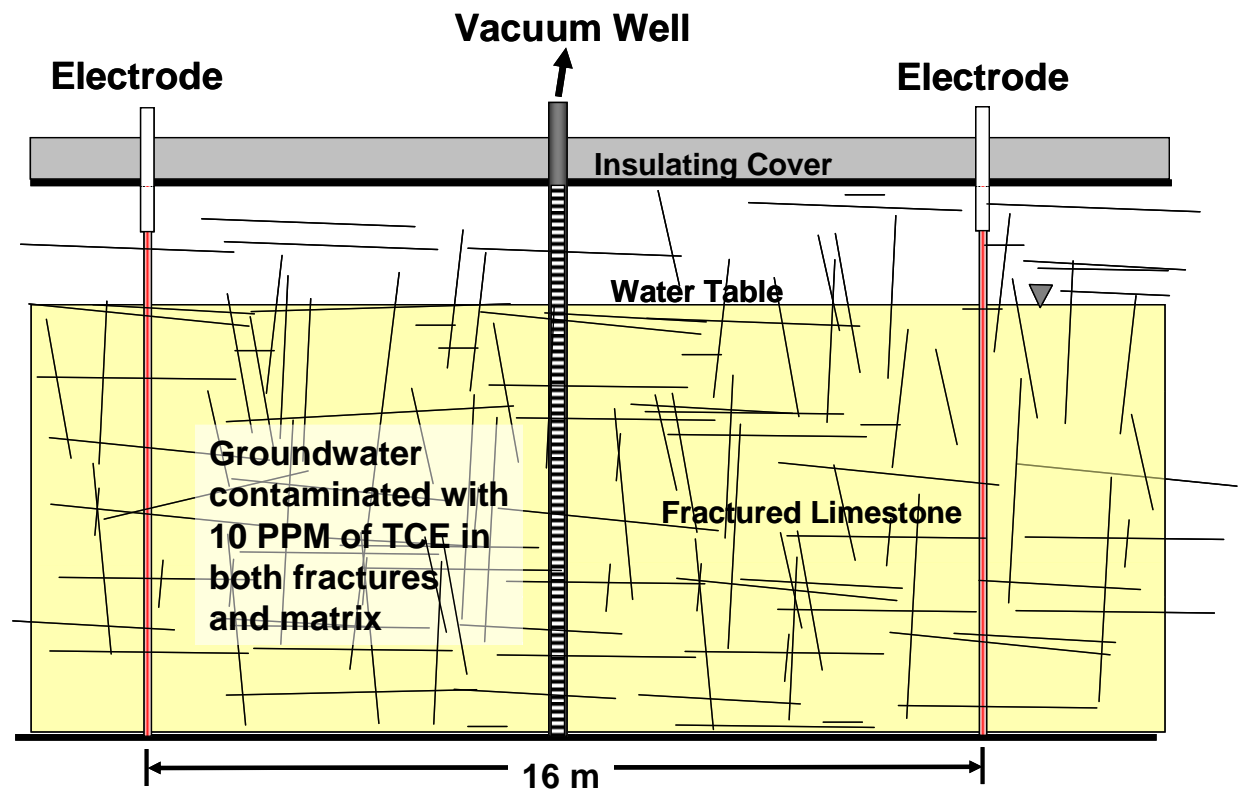
Each gridblock is subdivided into a fracture element, and multiple nested matrix elements. The fracture and matrix elements are locally connected to each other in 1-D

Field Simulation Example

Idealized field scale simulation – single element of a repeated 6-phase electrical heating pattern.

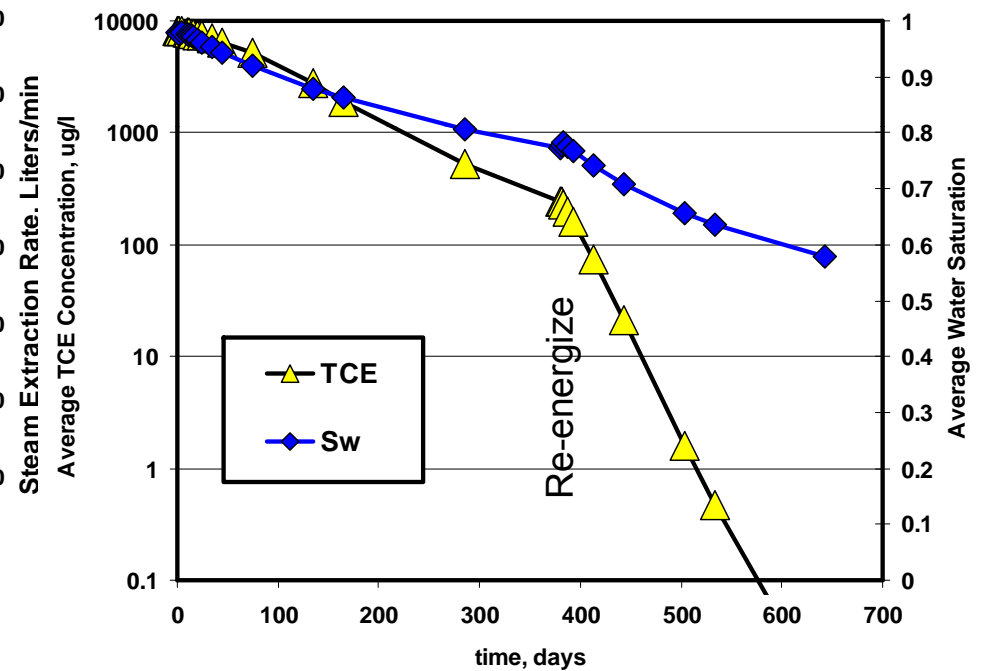
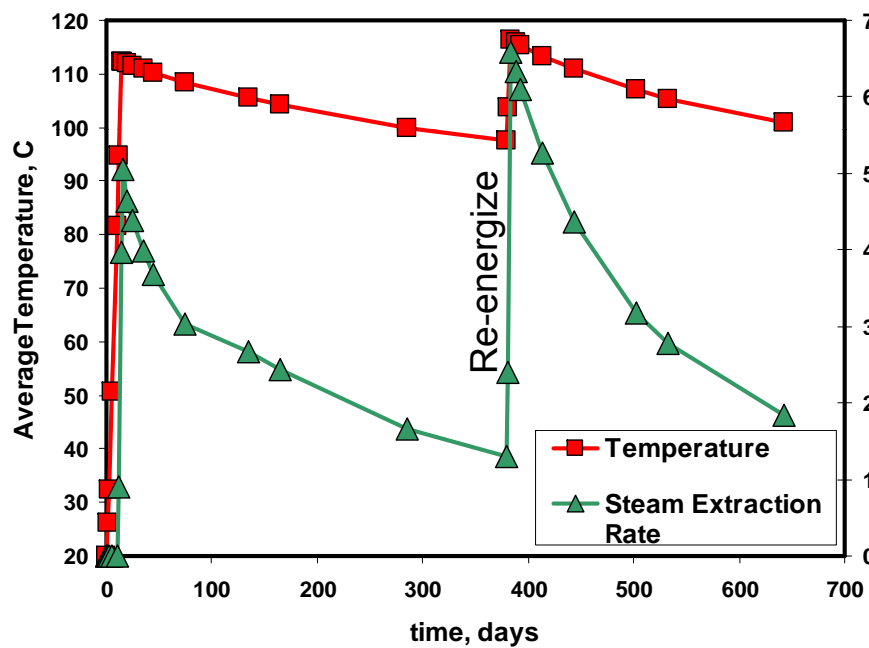
3-D orthogonal set of 200 micron fractures with 1m spacing, matrix $k=10^{-15} \text{ m}^2$; model uses MINC for matrix blocks.

Add 800 kW power for 15 days, then pump vacuum well at 0.5 ATM for 1 year. Re-energize for 3 days and pump vacuum well for another year





Simulation Result





Summary

- Experiments and simulations show good removal of volatile contaminants with about 40-50% removal of pore water by thermal treatment
- Several numerical models are available for simulating thermal remediation. These codes should be able to capture the key heat and mass transfer effects that occur.
- Field scale models of fractured systems are challenging because of scale effects and the strong interaction between the fractures and matrix
- MINC discretization appears to be the most practical way to setup most large field simulations

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KNOXVILLE

Departments of Microbiology and of Civil & Environmental Engineering
Oak Ridge National Laboratory, Environmental Sciences Division



Effects of Thermal Treatment on the Microbial Reductive Dechlorination Process

Frank E. Löffler



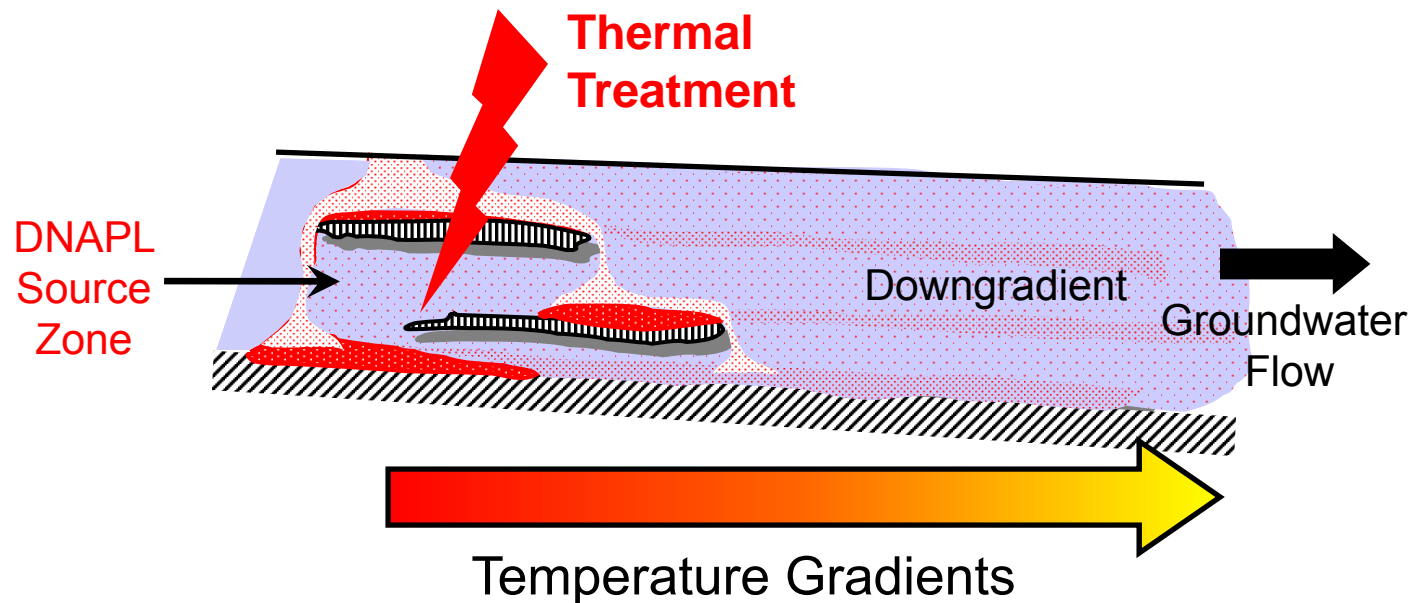
SERDP
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ESTCP



Microbial Reductive Dechlorination at Elevated T





Key Questions

1. Are reductively dechlorinating (i.e., organohalide-respiring) bacteria active at elevated temperatures?
2. Do reductively dechlorinating bacteria recover activity following exposure to elevated temperatures?
3. Does thermal treatment increase soil organic carbon (i.e., electron donor) bioavailability to sustain the reductive dechlorination process?
4. Does thermal treatment provide opportunities for post-treatment bioremediation to control residual contaminants?

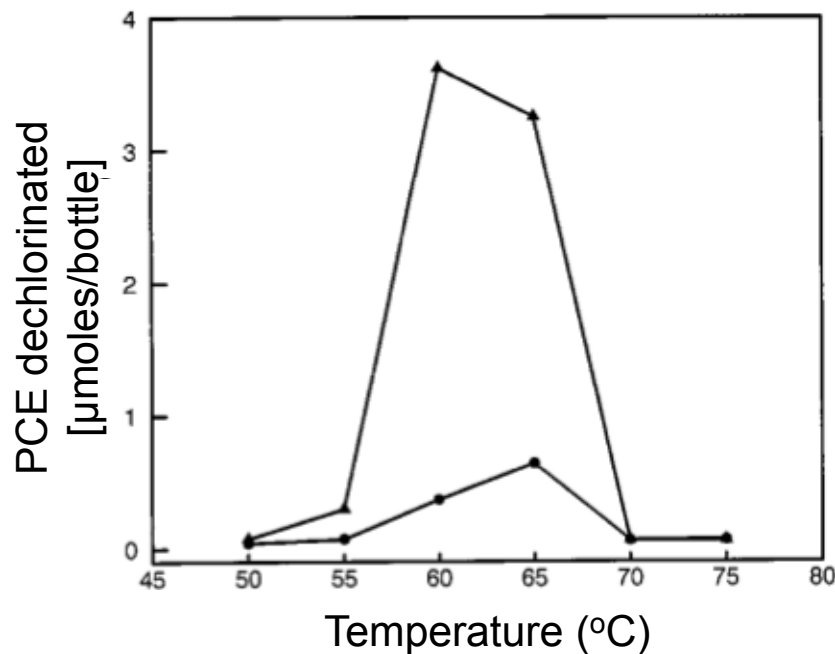


1. Microbial Reductive Dechlorination at Elevated T

- Reductive dechlorination of chlorinated solvents demonstrated at mesophilic temperatures (10-35 °C)
- Occurs in cold (4 °C) aquifers
(Bradley et al. 2005, Appl. Environ. Microbiol. 71:6414-6417)
- A thermophilic PCE-to-*cis*-DCE-dechlorinating mixed culture containing a *Dehalobacter* sp. obtained from Rhine River sediment (60-65 °C)
(Kengen et al. 1999, Appl. Environ. Microbiol. 65:2312-2316)
- Enrichment of PCE dechlorinators from geothermal areas not successful (unpubl. results)
- Screening of metagenome libraries established with DNA from geothermal environments did not detect reductive dehalogenase genes (unpubl. results)



Microbial Reductive Dechlorination at Elevated T

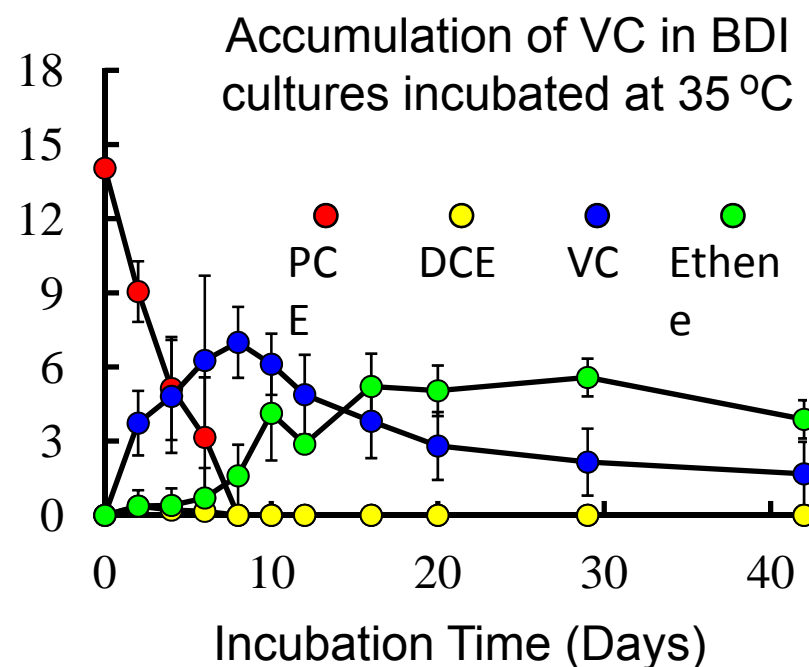
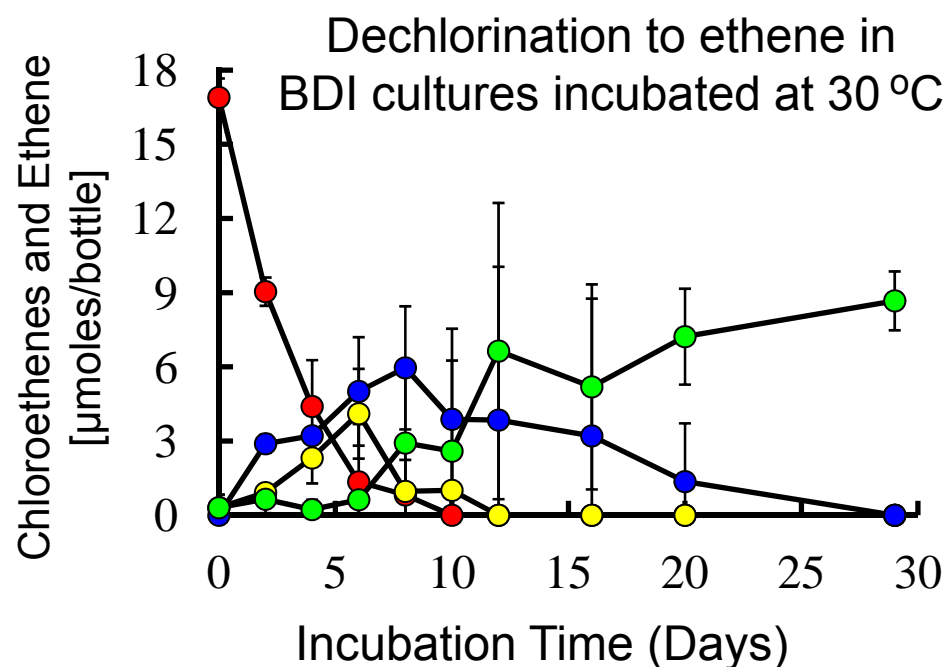


An enrichment culture derived from Rhine River sediment dechlorinated PCE to *cis*-DCE at 60 °C. A bacterium related to *Dehalobacter* was detected.

Kengen et al. 1999, Appl. Environ. Microbiol. 65:2312-2316

Reductive Dechlorination at Elevated T

Laboratory experiments with the PCE-to-ethene-dechlorinating consortium BDI



➡ No dechlorination at 40 °C
Potential for VC accumulation

Fletcher et al. 2011, ES&T
45:712-718



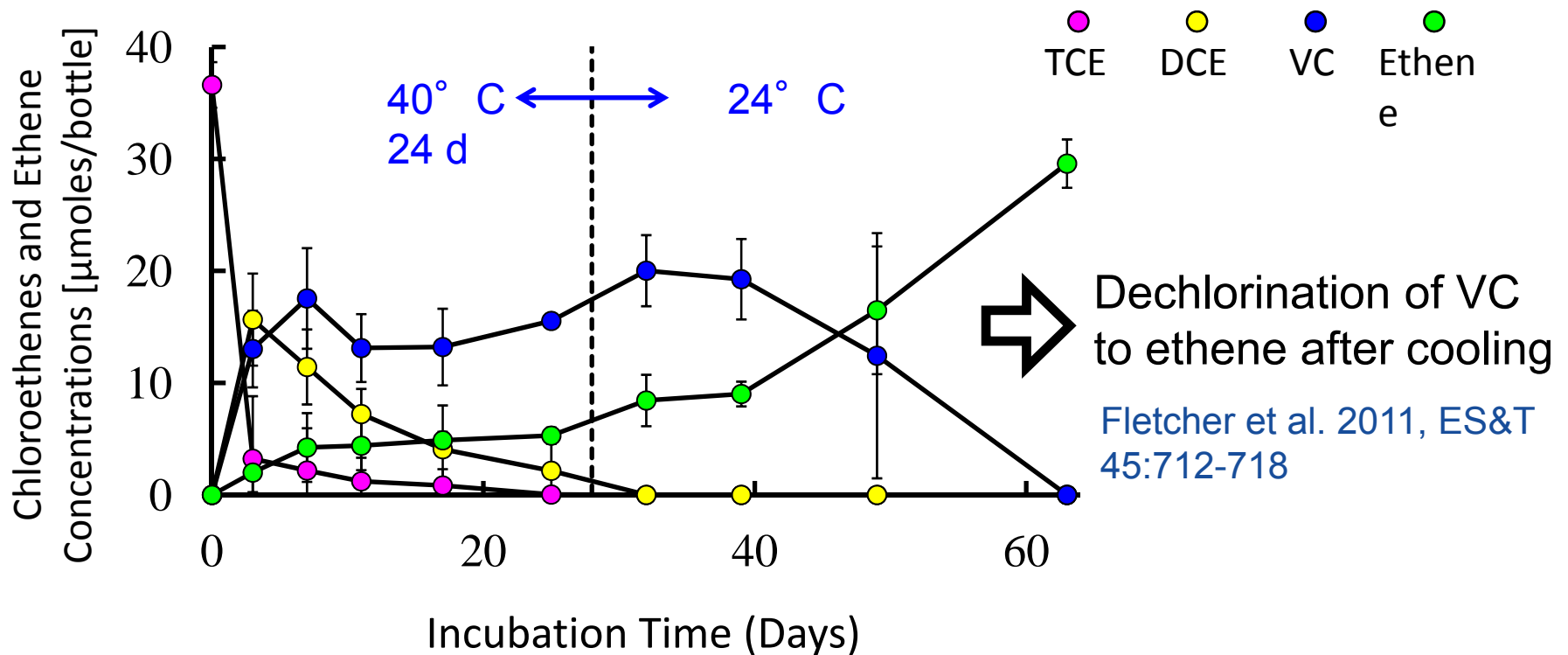
1. Microbial Reductive Dechlorination at Elevated T

- A single study reports reductive dechlorination of PCE to *cis*-DCE at temperatures of 60-65°C. This culture was derived from a “cold” river sediment.
- Search for thermophilic microbes capable of reductive dechlorination has not been successful to date. The efforts to date were limited in scope and the search should continue.
- Metagenome information is currently generated from many environments, including thermophilic habitats. Screening of these data sets for reductive dehalogenase genes will reveal their presence in thermophilic environments and can guide enrichment efforts.

2. Recovery of Reductive Dechlorination Activity

Laboratory experiments with the PCE-to-ethene-dechlorinating consortium BDI

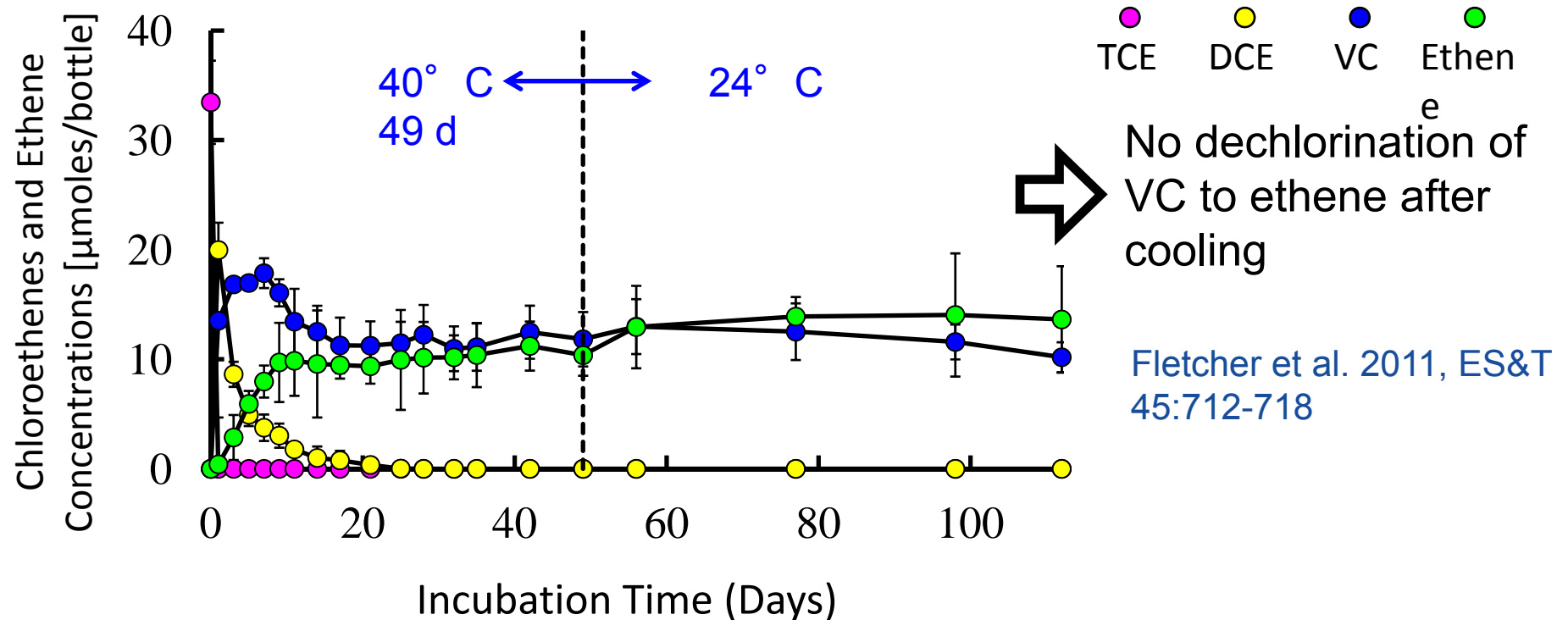
Incubation at 40°C for 24 days prior to cooling to 24°C



2. Recovery of Reductive Dechlorination Activity

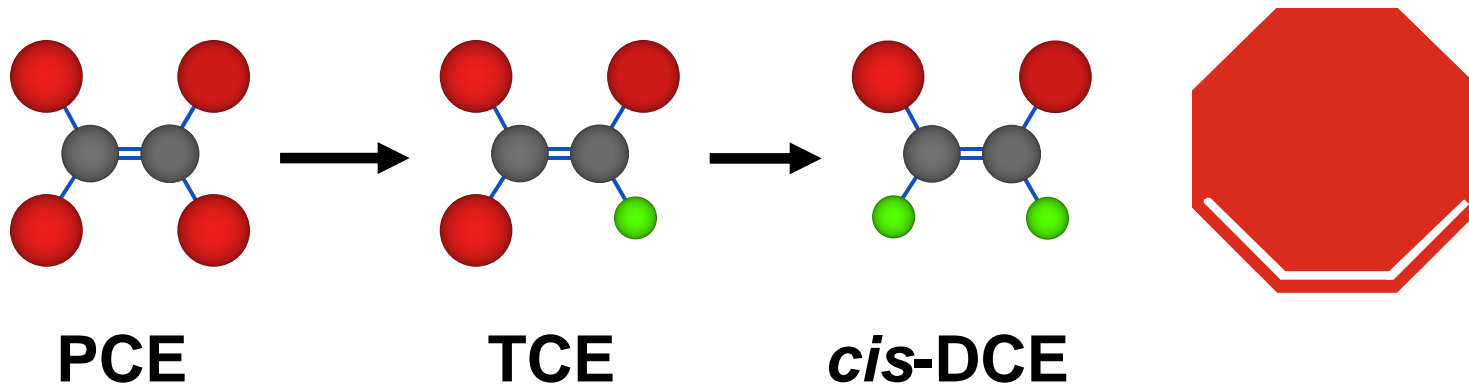
Laboratory experiments with the PCE-to-ethene-dechlorinating consortium BDI

Incubation at 40°C for 49 days prior to cooling to 24°C





2. Recovery of Reductive Dechlorination Activity



Sulfurospirillum, *Desulfitobacterium*, *Dehalobacter*, *Desulfuromonas*, *Geobacter*, ***Clostridium***

Isolation and Characterization of a Tetrachloroethylene
Dechlorinating Bacterium, *Clostridium bifermentans* DPH-1
Chang et al. 2000, J. Biosci. Bioeng. 89:489-491



A PCE-dechlorinating
spore former would be
able to survive high T



Resolution of Culture *Clostridium bifermentans* DPH-1 into
Two Populations, a *Clostridium* sp. and Tetrachloroethene-
Dechlorinating *Desulfitobacterium hafniense* Strain JH1.
Fletcher et al. 2008, Appl. Environ. Microbiol. 74:6141-6143



No PCE-dechlorinating
spore formers have
been identified to date



2. Recovery of Reductive Dechlorination Activity

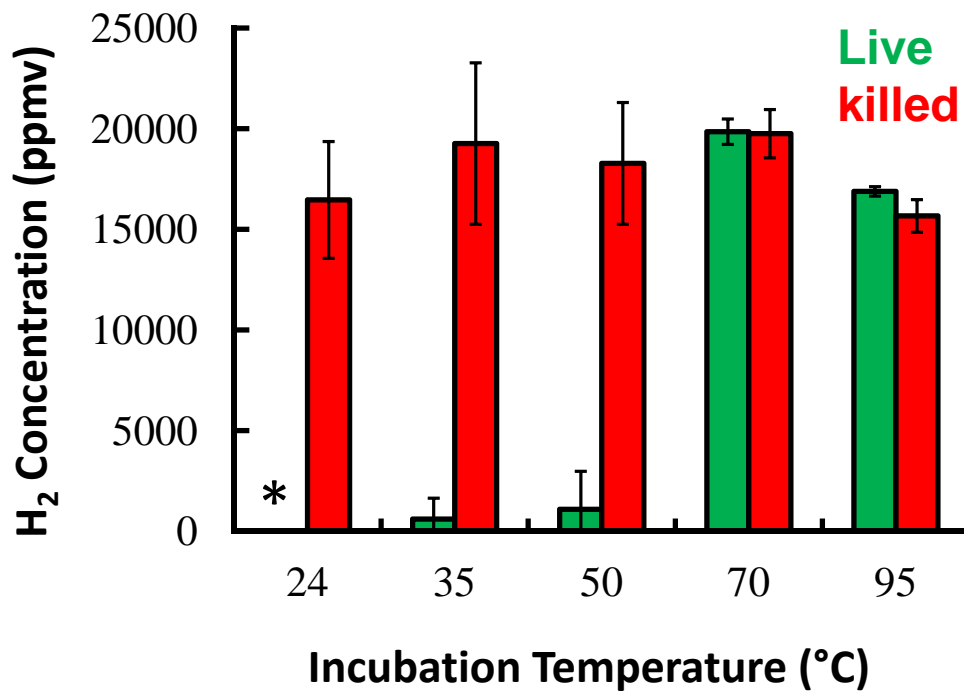
- No reductive dechlorination activity recovered from cultures incubated at temperatures $>40^{\circ}\text{C}$
- Duration of exposure to elevated temperatures affects recovery of dechlorination activity
- The VC-to-ethene dechlorination step is most susceptible to heat inactivation
 - ➔ Increased potential for VC accumulation
- No spore-forming chlorinated solvent dechlorinators have been described



3. Release of ED for Reductive Dechlorination During/Following Thermal Treatment

Microcosm experiments with Ft. Lewis soil

Hydrogen production at different incubation temperatures

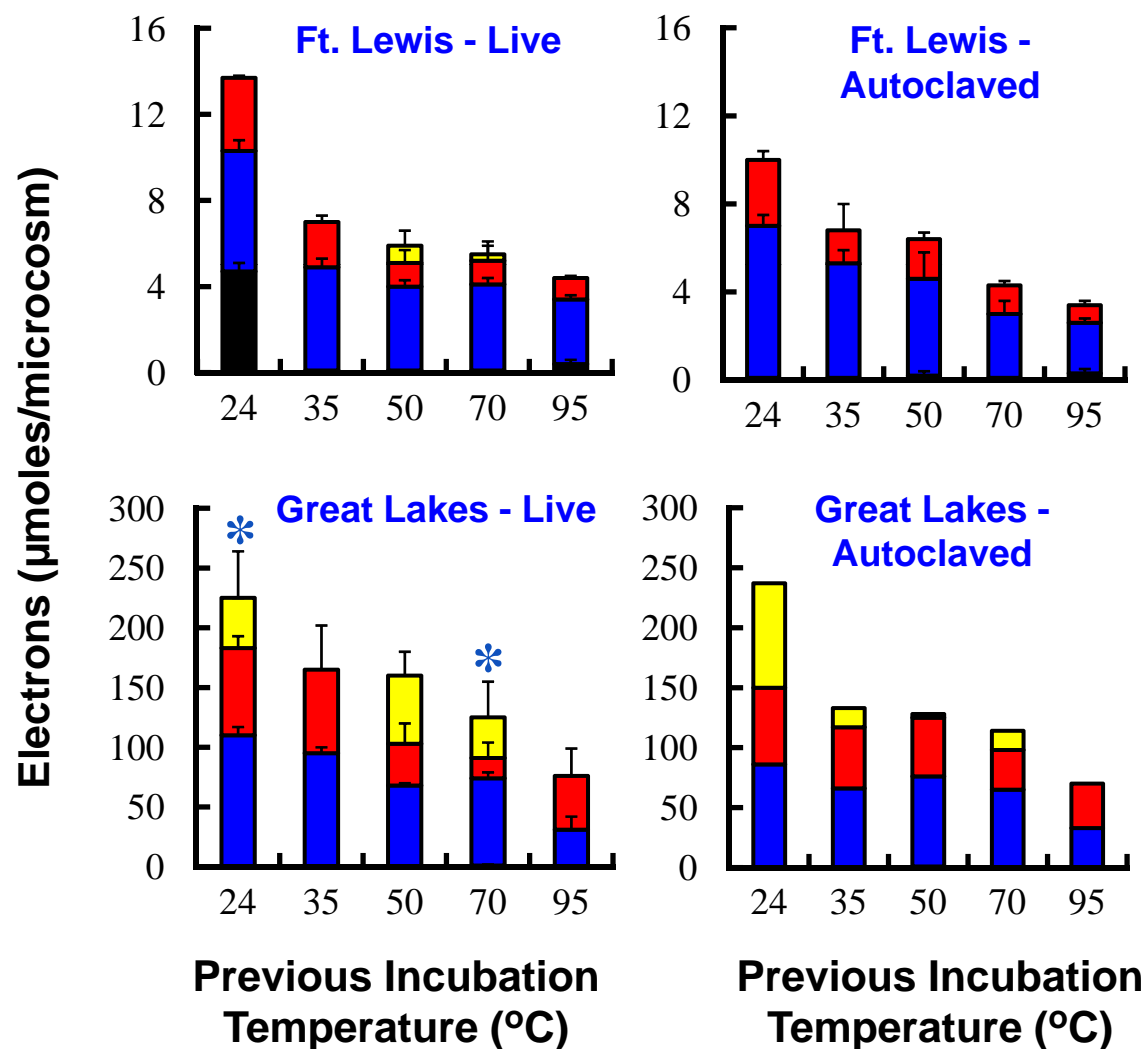


H₂ concentrations in live and autoclaved Ft. Lewis microcosms after 28 days of incubation

Fletcher, Water Research. In Press.

doi:10.1016/j.watres.2011.09.033

3. Release of ED for Reductive Dechlorination

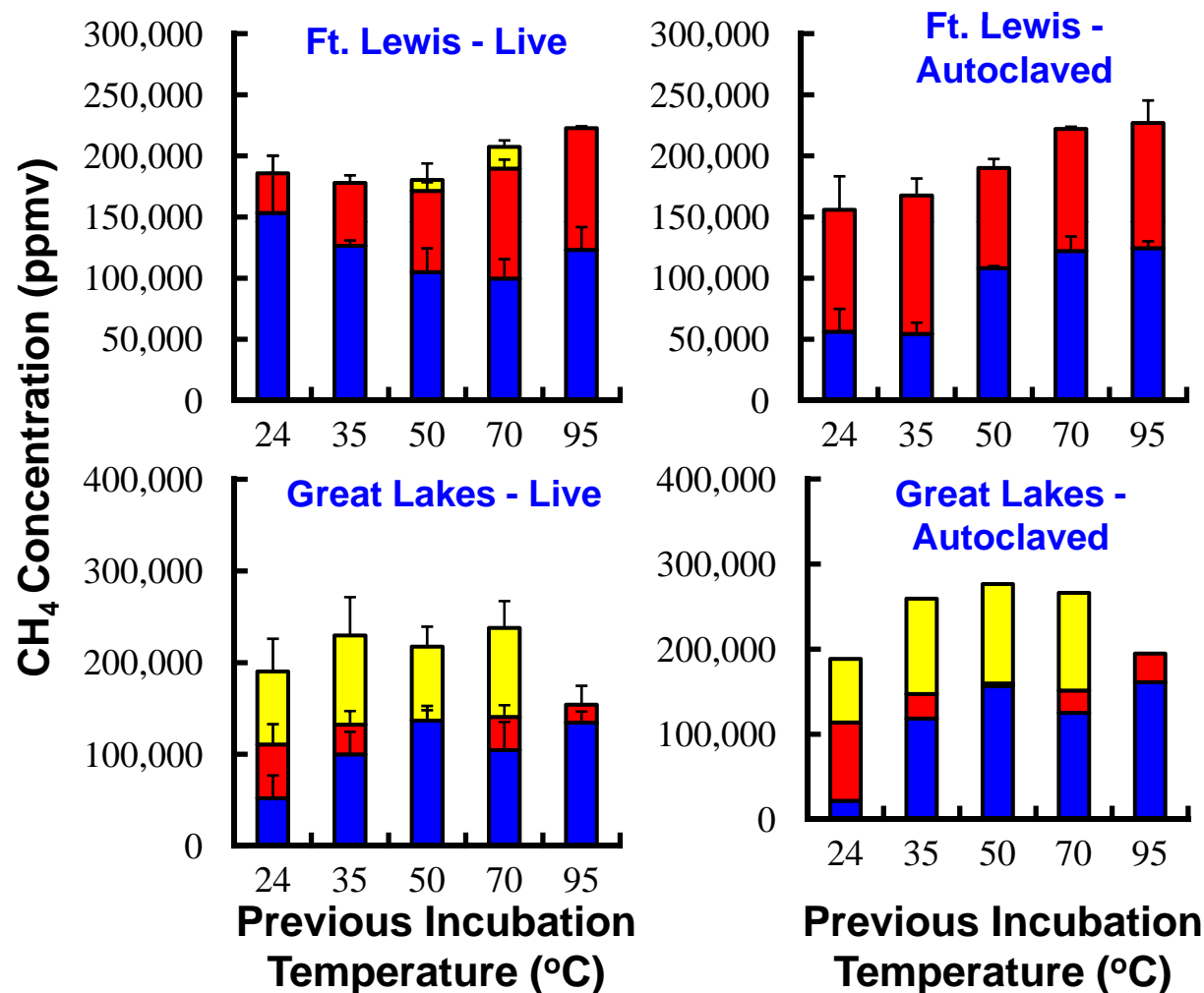


Microcosms established from Ft. Lewis, WA, and Great Lakes, IL

Depicted is the **electron donor (ED) consumption** in **reductive dechlorination** following thermal treatment.

➔ More reducing equivalents directed towards reductive dechlorination in microcosms that had been incubated at lower temperatures

3. Release of ED for Reductive Dechlorination



Microcosms established from Ft. Lewis, WA, and Great Lakes, IL

Depicted is the **electron donor (ED) consumption** in **methane formation** following thermal treatment.

- Prior to biostimulation
- After biostimulation I
- After biostimulation II

The majority of reducing equivalents released from the soil matrix during heat treatment are consumed in methanogenesis rather than reductive dechlorination (i.e., <0.1%).



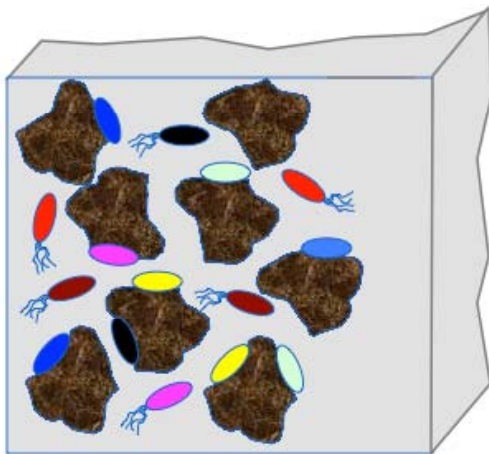
3. Release of ED for Reductive Dechlorination

- Thermal treatment increased the hydrogen flux
- At the two sites investigated, the amount of reducing equivalents consumed in reductive dechlorination negatively correlated with previous incubation temperature (i.e., fewer electrons consumed in microcosms previously incubated at higher temperature)
- At both sites, biostimulation (i.e., the addition of electron donor) was required to sustain reductive dechlorination and ethene formation
- The majority of reducing equivalents was consumed in methanogenesis

4. Opportunities for Enhanced Post-Thermal Treatment Bioremediation

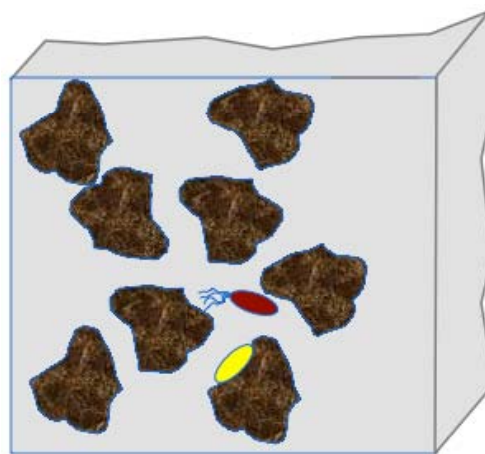
- Bioaugmentation with non-methanogenic consortia can increase the efficiency of the reductive dechlorination process (i.e., a greater fraction of the available reducing equivalents will be consumed in reductive dechlorination)

Before ΔT



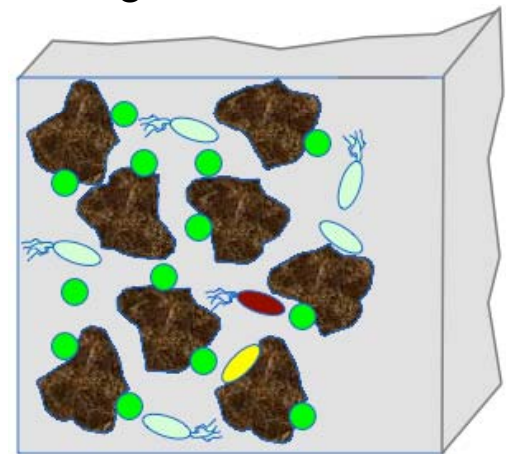
Niches Occupied

After ΔT



Open Niches

Bioaugmentation after ΔT



Colonialization of open niches by bacteria in the inoculum



Conclusions

- Residual contamination often remains following thermal treatment
- Subsequent bioremediation is a promising polishing step to meet remediation goals → Combined Remedy Approach
- The known bacteria capable of reductive dechlorination cannot tolerate elevated temperatures
- The VC-to-ethene step is most susceptible to temperature inhibition
- Thermal treatment increases electron donor (e.g., hydrogen) flux
- The majority of the hydrogen is consumed by methanogens
- Thermal treatment may offer unique opportunities for enhanced bioremediation by using bioaugmentation inocula not containing methanogens

Acknowledgements

- Kelly Fletcher (former PhD student)
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- Jed Costanza (U.S. EPA)
- Natalie Capiro (Tufts University)
- Kurt Pennell (Tufts University)

SERDP Projects ER-1419 and ER-1586

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